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SURFACTANT EFFECTS ON PESTICIDE PHOTOCHEMISTRY IN WATER AND SOIL

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FOREWORD

Environmental protection efforts are increasingly directed towards the prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Processes Branch studies the microbiological, chemical, and physicochemical processes that control the transport, transformation, and impact of pollutants in soil and water.

The toxicity and persistence of pesticides and their decomposition products are problems of major concern to those concerned with environmental quality. Unfortunately, much information is lacking on the fate of these materials. The study reported here investigates the photodecomposition of three pesticides on soil surfaces and examines the influence that surfactants have on the photodecomposition of these pesticides in aqueous solutions. The report contributes to the overall perspective of the pesticide problem and provides quantitative rate data that can be used in environmental modeling studies.

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ABSTRACT

The effects of surfactants on the photochemical decomposition of selected pesticides are examined both in aqueous solution and on selected soil surfaces. Typical surfactants usually enhance the rate of pesticide photodecomposition. In solution, increased quantum efficiencies and increased overlap with available solar irradiation are observed. In addition, surfactants enhance the solubility of otherwise sparingly soluble pesticides. Photodecomposition on soil surfaces is inefficient. Surfactants enhance the rates of decomposition in certain cases on soil surfaces, but the effects do not appear to be sufficiently large to make such a mode of decomposition competitive. It has been postulated that the reason pesticide photochemistry on soils is so inefficient is that excitation energy is lost to pigments in the soil. This report was submitted in fulfillment of Grant No. R-802959 by The University of Georgia under the sponsorship of the U.S. Environmental Protection Agency. Work was completed as of November 30, 1977.

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SECTION 1

CONCLUSIONS

Surfactants increase the solubility of otherwise sparingly soluble pesticides thereby increasing the likelihood of their decomposition in aqueous solution.

Surfactants alter the light absorbing characteristics of certain pesticides by generally shifting the absorption bands to lower energy. This alteration has the effect of increasing the overlap of the absorption band and the solar radiance spectrum.

In certain cases, surfactants enhance the quantum efficiency of pesticide photodecomposition in solution. In combination with above-mentioned factors, a significant enhancement in the "rate" of photodecomposition is realized.

The photochemical decomposition of these pesticides on soils is far less efficient than in solution. Although detergents and soil water have been shown to enhance the rate of decomposition on soils in certain cases, it is unlikely that this mode of decomposition will be environmentally important unless actual aqueous solutions of the pesticides are formed. For certain pesticides which absorb strongly in the near UV and visible spectral regions, the rates of photolysis might be sufficiently fast (in spite of low quantum efficiencies) to invalidate this conclusion. It has been postulated that loss of excitation energy to pigments in the soil may be responsible for the slow rates of photodecomposition observed. Fluorescence experiments on soil surfaces are consistent with this hypothesis.

Experiments have verified that photodecomposition on soil surfaces would occur only at the outermost surface of the soil. Thus any penetration by a pesticide into the soil would diminish further the already slow photodecomposition process.

SECTION 2

RECOMMENDATIONS

It appears that sunlight induced decomposition of pesticides is likely to be important only in solution (and perhaps in the atmosphere) rather than on soil surfaces. Therefore, the rate and nature of pesticide photodecomposition should be studied in aqueous solution in the presence of the formulating agent. In addition, naturally occurring surfactants and emulsifying agents may exert a similar effect in accelerating pesticide decomposition in water runoff conditions and should be examined.

SECTION III

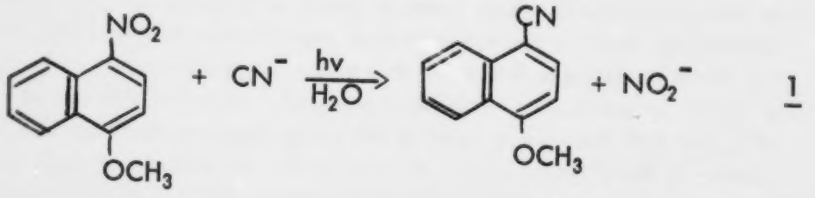
INTRODUCTION

A problem of major concern to the environmentalist is the fate of pesticides both as persistent species and with regard to the toxicity and persistence of their decomposition products.[1] Contributing to the complexity of the problem is the increasing variety of types of pesticides that are replacing those such as DDT for which data show intolerable levels of persistence and toxicity.[2] An alarming aspect of employing new pesticides is the lack of reliable information concerning the overall cumulative effect on the environment of their persistence and of the toxicity and persistence of their decomposition products.[3,4] The problem is likely to become more severe, but even now briad attempts to trace the fate of pesticides account for only some 10% of that which has been applied.[5]

The action of sunlight on pesticides in the field, in air-suspended droplets,[6] and in water runoff is likely to be an important mode of pesticidal decomposition in competition with microbial decomposition and to some extent, with ordinary chemical decomposition. Ultimately to obtain an intelligent perspective of the pesticide problem an overall picture must be assembled that includes: (1) the probable rates of decomposition by these various means as determined under conditions closely resembling those in the environment and (2) knowledge of the decomposition products and their subsequent fate. To this end, numerous studies of the photochemistry of a variety of pesticides have been pursued. Many of these studies are subject to the criticism that they were carried out under laboratory conditions bearing little resemblance to those found in the environment. In defense of such studies, however, it has been pointed out numerous times that analytical difficulties and other problems make studies of pesticide photochemistry in the "field" exceedingly complicated.[7] The purpose of this study was to consider the effects of such environmental perturbants, namely surfactants (also called detergents),and their role in altering pesticidal photochemical behavior. Surfactants enter the environment through a variety of natural sources and as water pollutants in waste effluent, but perhaps the most important source of surfactants with regard to pesticides is the simultaneous co-application of pesticides and surfactants in pesticidal formulations. The effect of surfactants and their aggregates (micelles) on chemical and photochemical reactions is a topic of intensive investigation.[8] Studies have shown that surfactants can dramatically alter the course of photochemical reactions.[9] Among the effects potentially pertinent to pesticide photochemistry are:

(1) Shifts of the ultraviolet absorption spectra of the photoreactant
(2) Dramatic enhancements of energy transfer efficiencies as manifested by by photosensitization and quenching of electronically excited states
(3) Changes in the quantum efficiencies of photochemical reactions
(4) Changes in the local molecular environment of the photoreactant that can alter the relative energies of excited states (resulting in entirely different observed photochemical products)
(5) Availability of locally high concentrations of micellar counterions capable of reacting with or quenching photoexcited states
(6) Sizeable enhancements in the water solubility of otherwise insoluble compounds
(7) Changes in the surface properties of solids through adsorption

Surfactants are quite remarkable species.[8] They usually consist of a long hydrocarbon chain with a polar or ionic functional group at one end. In spite of their appreciable hydrocarbon content, they are usually soluble in water to an almost unlimited extent and, in turn, solubilize non-polar organic compounds that would otherwise be highly insoluble in water. A variety of chemical reactions have been studied in aqueous solutions containing surfactants, and the "catalytic" effects of the micelles on reaction rates can be quite striking. The wide variety of examples in the literature are too numerous to summarize here, but recent reviews are available in References 8, 10 and 11. An example we have previously observed will serve to illustrate the remarkable effects possible.[9] The photochemical reaction in equation 1 has a quantum yield in the presence of 1×10^{-2} M concentration of the cationic surfactant hexadecyltrimethylammonium bromide that is at least 6800 times that observed in the absence of the detergent. This dramatic effect is a result of primarily



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two features of the surfactant micelle: (1) its ability to efficiently organize both reactants into a common region of the solution thereby providing the photoexcited nitroaromatic with a highly effective concentration of cyanide ion and (2) its "solvent" effect on the micellized aromatic that in this case, alters the nature of the lowest-lying excited state. In contrast, the anionic surfactant sodium lauryl sulfate completely insulates the micellized nitroaromatic from the anionic nucleophiles and inhibits such photoreactions.[9] For example, similar substitution reactions of p-nitrophenyl decyl ether are inhibited by a factor of at least 200.

Significant changes in the ultraviolet and visible absorption spectra of compounds solubilized by micelles have been observed.[8] The effects arise from the local

solvent and electrostatic character of the micelle and are, of course, most commonly observed for compounds that exhibit a sensitivity to solvent shifts. Another typical case for which spectral shifts are observed arises from changes in acid-base equilibria of dissolved materials. For example, α-naphthol (a decomposition product of the pesticide Sevin) exhibits a large increase in observed pKa (ΔpKa= 1.2) in the presence of even nonionic detergents.[12]

Co-solubilization of two or more substrates by surfactant micelles can have dramatic effects on the efficiency of biomolecular reactions particularly those involving short-lived excited states. This is illustrated by the following case of very efficient energy transfer. Singhal and coworkers[13] showed that, in aqueous solution containing 1×10^{-5} M methylene blue, 1×10^{-5} M thionine and 3×10^{-3}M sodium lauryl sulfate, direct excitation of thionine resulted in sensitization of methylene blue fluorescence with an efficiency of ca. 90% under these conditions. In the absence of the surfactant, no detectable energy transfer is observed.

The concentration of a surfactant is a crucial factor in the sense that below the well-defined critical-micelle-concentration (cmc) surfactants are monomeric and behave as simple salts (ionic) or organic solutes (non-ionic).[8] At the cmc, through a process somewhat analogous to precipitation, micellar aggregates (typically consisting of 50-100 monomers) are formed. It is the micelle that exerts these effects on dissolved substrates. At concentrations above the cmc, the number of micelles increases, but no significant change in the character of the micelle occurs unless high concentrations (typically >0.1 M) are present. The capacity of the micelle to solubilize otherwise sparingly soluble substrates will, of course, increase with increasing "micelle" concentration, but the "catalytic" effects of micelles on chemical or photochemical reactions are generally rather insensitive to surfactant concentrations above the cmc (unless co-solubilization of two reactive substrates is required). The surfactant concentrations employed in the following study were all above the cmc values for the surfactants used. The cmc values for hexadecyltrimethylammonium bromide (HDTBr), sodium dodecyl sulfate (SDS) and Brij 35 are 9×10^{-4}M, 8×10^{-3} M and 7×10^{-5}M, respectively.[8] There is evidence in the literature that, for certain cases, micellar effects can occur below the cmc. This is ostensibly due to complexes between surfactant and substrate and to substrate-induced micellization.[14,15]

The degree to which surfactants (the term is used here in a broad sense to cover all types of amphiphilic molecules such as detergents, soaps, bile acid salts and membrane constituents that exhibit surface active properties and form micelles in solution) perturb the photochemistry of pesticides is a factor that deserves considerable attention. An understanding of these effects is becoming increasingly more important as the use of surfactants in pesticidal formulations increases.[16] Studies concerning the penetration ability, translocation, effective toxicity, biological activity, and water solubility of pesticides as influenced by surfactant formulations attest to the practical significance of pesticide-surfactant interactions.[16-21] For example, Lichtenstein has found that surfactants increase the persistence and

toxicity of parathion and diazinon in soils.[21] Rosen has discussed several cases of pesticides with ultraviolet absorption bands that do not overlap with the spectrum of available solar light but are readily photolyzed by sunlight.[7] Explanations of this apparent paradox include sensitization by impurities or oxidation products of the pesticides and possible changes in the absorption spectrum resulting from surface adsorption of the pesticide. In addition, however, spectral shifts caused by surfactants can significantly alter the fraction of light directly absorbed by the pesticide and must be considered.

The important of differing surface characteristics on the photochemistry of pesticides has been discussed by Plimmer.[22] The interesting observation that a series of methylcarbamates were readily photolyzed on glass or leaf surfaces but not on silica gel surfaces was noted. Rosen observed a similar case in the photochemistry of the pyrethroid SBP-1382 and was left with the dismaying conclusion that, if studies between glass and silica gel surfaces differ significantly, any extrapolation of these studies to predict photochemistry on soil surfaces must be risky at best.[7] Considerable value, however, is derived from these observations in that we are made aware of the possible sensitivity of certain pesticide photochemistry to very specific surface effects. Clearly the specific character of various soils differs as much if not more from one sample to the next as does glass from silica gel. Furthermore, the character of soil surfaces might be expected to change in the presence of surfactants. The question of the importance of pesticide photolysis on soil surfaces has not been dealt with in any systematic manner although several reports have indicated that pesticide photochemistry does indeed occur on soils. Lichtenstein and coworkers have observed evidence for photochemical transofmrations of pesticides on soils.[23] Woodrow, Crosby and coworkers have observed a rapid conversion of parathion to paraoxon induced by UV light on orchard soil surfaces.[24] Baker and Applegate found that UV light accelerated the breakdown of parathion and DDT on soil surfaces.[25] They found no paraoxon (or p-nitrophenol) as photoproducts, however.

One of the two major objectives of the following study was to investigate the photodecomposition of several pesticides on soil surfaces by systematically varying several parameters likely to influence the photolysis "rates". The other principal objective was to determine the influence that surfactants have on the photodecomposition of these pesticides in aqueous solution. For both systems it was intended to obtain quantitative rate data that could be used in environmental modelling studies. A secondary objective involving the isolation and identification of all photoproducts was hampered by numerous experimental difficulties and only indirect evidence for the nature of the photoproducts was obtained.

SECTION IV

RESULTS AND DISCUSSION

AQUEOUS PHASE STUDIES

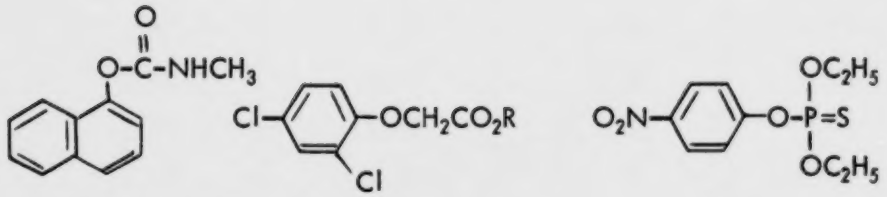
Absorption Spectra

We have examined the effects of three different types of surfactants--cationic-hexadecyltrimethylammonium bromide (HDTBr), I; anionic-sodium dodecylsulfate (SDS), II; and nonionic-Brij 35, III--on the solubilization and electronic absorption spectra of Sevin, IV, 2,4-D esters, V, and parathion, VI, in aqueous solution (Figure 1). We have not determined the upper limit of solubility of these pesticides

$$CH_3(CH_2)_{15}\overset{+}{N}(CH_3)_3Br^- \qquad I$$

$$CH_3(CH_2)_{11}\text{-}OSO_3^-Na^+ \qquad II$$

$$CH_3(CH_2)_{11}O\text{-}(CH_2CH_2O)_{23}\text{-}OH \qquad III$$



IV V VI

Figure 1. Surfactants and pesticides used in study.

in detergent solutions, but it is clear that solubility limits would not be reached by any reasonable environmental concentrations. For example, we have prepared (with no difficulty) detergent solutions of the sparingly soluble butoxyethyl ester of 2,4-D in concentrations as high as 10^{-3}M. This compares with an aqueous saturation solubility of ca. 4×10^{-5}M.

Surfactants shift the UV spectra of these pesticides significantly to the red. The spectra for 2,4-D resemble those in hexane and methanol. The overall influence in the case of 2,4-D esters is far more important than for Sevin or parathion in that the natural overlap of the spectra with the available sunlight is marginal for 2,4-D. At pertinent wavelengths (Tables 1, 2 and 3), it is seen that the increase in net absorption at wavelengths greater than 290 nm is significant.

An interesting effect was observed for solutions of parathion. The wavelength absorption maximum for parathion varies from 269 nm in n-hexane to 276 nm in water (273 nm in methanol; 273 nm in acetonitrile and 274 nm in 50% aqueous methanol). It is reasonable to expect that the addition of detergents to aqueous solutions would result in absorption shifts toward those values found for less polar solvents; however, the absorption maxima of parathion in 0.05 M HDTBr and 0.05 M SDS were found to be 280 and 281 nm, respectively. An explanation for this unusual effect may involve a specific interaction between the thiophosphate ester group with the ionic head groups

Table 1. EXTINCTION COEFFICIENT FOR METHYL ESTER OF 2,4-D

	Molar Extinction Coefficient (ℓ-mole^{-1}-cm^{-1})			
λnm	H_2O	1×10^{-2} M HDTBr (cationic)	5×10^{-2} M SDS (anionic)	1×10^{-3} M Brij 35 (nonionic)
297.5	236	499	407	341
300	78.7	197	171	131
302.5	52.5	78.7	78.7	65.6
305	39.4	39.4	52.5	39.4
307.5	39.4	26.2	39.4	26.2
310	26.2	13.1	26.2	26.2
312.5	26.2	0	26.2	13.1
315	13.1	0	26.2	13.1
317.5	13.1	0	13.1	13.1
320	0		13.1	0
322.5	0		0	0
325			0	
327.5				
330				

Table 2. EXTINCTION COEFFICIENT FOR SEVIN

λnm	Molar Extinction Coefficient (ℓ-mole^{-1}-cm^{-1})			
	H_2O	1×10^{-2} M HDTBr (cationic)	5×10^{-2} M SDS (anionic)	1×10^{-3} M Brij 35 (nonionic)
297.5	1.41×10^3	2.45×10^3	1.88×10^3	1.64×10^3
300	9.3×10^2	1.73×10^3	1.21×10^3	1.11×10^3
302.5	737	1.32×10^3	880	876
305	529	1.04×10^3	649	659
307.5	409	803	478	511
310	351	683	386	444
312.5	378	622	375	435
315	259	529	305	320
317.5	236	440	239	228
320	112	332	143	157
322.5	57.9	247	69.5	103
325	29.0	216	38.6	66.5
327.5	19.3	134	23.2	36.3
330	13.2	57.9	15.9[a]	18.1
332.5	9.3[a]	30.9	11.0[a]	9.1
335	6.6[a]	15.4	7.9[a]	5.2[a]
337.5	4.6[a]	15.4	5.4[a]	3.2[a]
340	3.2[a]	11.6	3.7[a]	2.9[a]
342.5		8.1[a]		
345		6.0[a]		
347.5		4.4[a]		
350		3.2[a]		
352.5				
355				
357.5				
360				

a) Calculated from logarithmic extrapolation.

Table 3. EXTINCTION COEFFICIENT FOR PARATHION

	Molar Extinction Coefficient (ℓ-mole^{-1}-cm^{-1})		
λnm	H_2O	5×10^{-2} M HDTBr	5×10^{-2} M SDS
297.5	4800	6250	6350
300	4500	5800	5850
302.5	4250	5150	5500
305	3750	4500	4800
307.5	3250	3800	4200
310	2750	3100	3700
312.5	2350	2900	3400
315	2000	2200	2800
317.5	1600	1850	2450
320	1550	1600	2100
322.5	1400	1450	1850
325	1200	1000	1650
327.5	1100	950	1500
330	950	900	1300
332.5	750	900	1250
335	700	800	1100
337.5	600	650	1000
340	550	600	950
342.5	550	550	900
345	500	500	800
347.5	500	500	750
350	400	450	650

of the micelles. Such an effect might allow greater interaction between the ring-substituted oxygen and the nitro group such as is found in p-nitroanisole (λ max: 317 nm).

Quantum Yield and Rate Studies

The "rate" of any photochemical reaction is intrinsically related to the intensity of the light source used, and, even though much of the data reported here are expressed in terms related to "rates", it must be understood that such values have meaning only with respect to the experimental conditions employed. Although these studies were carried out under controlled laboratory conditions, it is desirable to relate the results to real environmental conditions. In order to do this, one must have detailed knowledge of the wavelength dependent intensities of the sources used (sunlight versus laboratory lamps) and the wavelength dependent extinction coefficients of the photochemical reactant. The common link between two such systems is the quantum efficiency, ϕ. The actual "rate" of a photochemical reaction is then given by equation 1.

$$\frac{-dc}{dt} = \phi \int I(\nu)\, a(\nu) d\nu \qquad (1)$$

where: I = wavelength dependent light intensity

a = wavelength and concentration dependent absorptivity of the reactant $a = 1-10^{-\ell \epsilon c}$ (ℓ is the pathlength, ϵ is the molar extinction coefficient, and c is the concentration of the photoreactant)

ϕ = quantum efficiency. This value is rarely wavelength dependent in condensed phases.

For those conditions in which the photoreactant does not completely (<99%) absorb the incident light, the function $a(\nu)$ is time-dependent. Under such circumstances, the course of the photolysis follows a first order dependence on the concentration of the photoreactant, and thus the "half-life" of the photoreaction is inversely proportional to the quantum yield as indicated in equation 2. The proportionality constant, k, embodies the characteristics of the overlap integral in equation 1.

$$t_{1/2} = \frac{k}{\phi} \qquad (2)$$

Solar insolation data as a function of geographical location, atmospheric conditions, time-of-day and season of year have been compiled by Zepp and coworkers[26] and used to calculate photolysis rates for pesticide photodecomposition using values of quantum efficiencies and extinction coefficients obtained from the laboratory. The agreement between empirically determined half-lives and those calculated has been excellent.[26,27] Data obtained in our studies have been treated accordingly to pre-

dict actual half-lives for photolysis in sunlight. These data are compiled in the apprendix and selected values given in Table 4. The quantum yields for disappearance of 2,4-D methyl ester and for Sevin were determined using optically matched solutions (at 290 nm) using 290 nm monochromatic light isolated with a monochromator on a conventional optical bench. The quantum yields for disappearance of parathion were measured using 313 nm light isolated from a medium pressure Hg arc filtered through a dichromate solution on a merry-go-round apparatus. Preliminary studies using the non-ionic surfactant Brij-35 resulted in extensive analytical interference from impurities in the detergent. Because our attempts to purify the surfactant by standard procedures[8] did not alleviate this problem and because, in virtually all known examples of micellar catalysis, the effects of non-ionic detergents are intermediate between the effects exerted by cationics and anionics[8], no further studies were undertaken.

The influence of detergents on the photolysis of 2,4-D methyl ester and Sevin can also be seen by examining spectral scans of the solutions taken after various photolysis periods. These are given in Figures 2-7. Of particular interest for 2,4-D are the clean isosbestic points at 279 and 298 nm for the solution containing the cationic detergent (Figure 2). For the solution containing the anionic detergent (Figure 4), secondary photodecomposition is apparent from the lack of isosbestic points, and for the solution in the absence of detergents (Figure 3) and overall increase in the absorption spectra, unlike either of the detergent solutions, occurs. Qualitatively different spectra scans were also obtained for the Sevin photolyses.

Table 4. CALCULATED PHOTOLYSIS HALF-LIVES FOR AQUEOUS SOLUTIONS OF 2,4-D METHYL ESTER, SEVIN AND PARATHION IRRADIATED BY SUNLIGHT

Pesticide	Solution	ϕ	Half-life (days)[a]
2,4-D Methyl ester	H_2O	0.06	62.
	0.01 M HDTBr	0.1	500.
	0.05 M SDS	0.1	21.
Sevin	H_2O	0.01	11.
	0.01 M HDTBr	0.03	1.2
	0.05 M SDS	0.01	9.6
Parathion	H_2O	0.0002	9.2
	0.05 M HDTBr	0.0006	2.9
	0.05 M SDS	0.001	1.3

a) Average on clear days during midsummer at 40°N latitude. See appendix for complete data.

Photodecomposition Products

The nature of the photoproducts obtained for the photolysis of 2,4-D esters in aqueous solution has been studied by several groups. Zepp and coworkers[27] have found that in dilute aqueous solution 2,4-D esters are converted to 2,4-dichlorophenol, the ester of 2-chloro-4-hydroxy-4-chlorophenoxyacetic acid, which rapidly lactonizes under the conditions of analysis (gas chromatography). At higher concentrations in aqueous solution (forming emulsions) or in organic solvents, Zepp and coworkers[27] found the ester of 4-chlorophenoxyacetic acid to be the major photoproduct along with some of the ester of 2-chlorophenoxyacetic acid. Crosby and coworkers have shown that the photolysis of 2,4-D acid in aqueous solution yields 2,4-dichlorophenol, 2-chloro-4-hydroxyphenoxyacetic acid and 4-chloro-2-hydroxyphenoxyacetic acid as primary photoproducts.[28] These undergo secondary photochemistry to ultimately produce humic-like materials. Binkley and Oakes have also studied photodecomposition of the esters of 2,4-D[29], but apparently at concentrations at which emulsions form because the photochemistry they observed is similar to that found by Zepp and coworkers in organic solvents and aqueous emulsions.

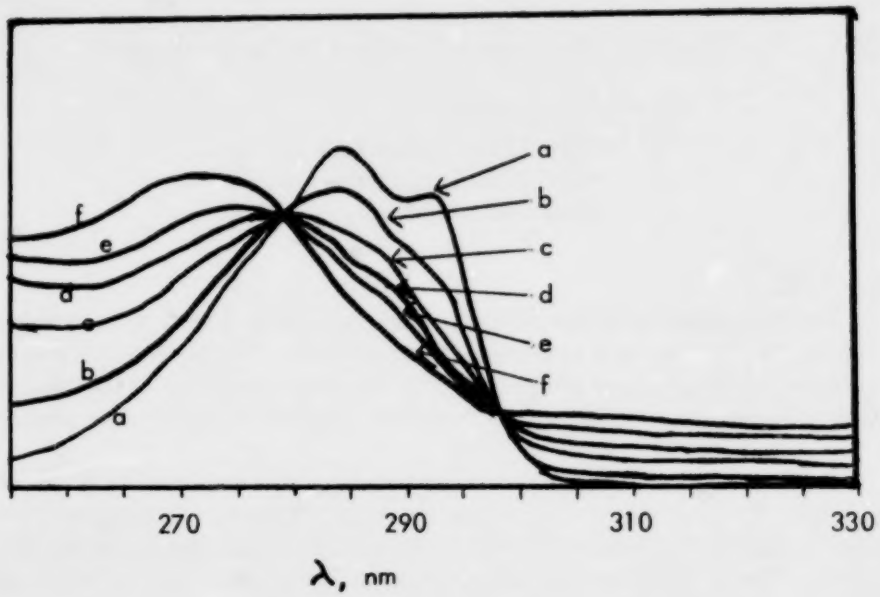


FIGURE 2 Photolysis of 2,4-D methyl ester with cationic detergent

- a initial spectrum
- b after 66 min photolysis period
- c after 120 min photolysis period
- d after 180 min photolysis period
- e after 240 min photolysis period
- f after ca. 360 min photolysis period

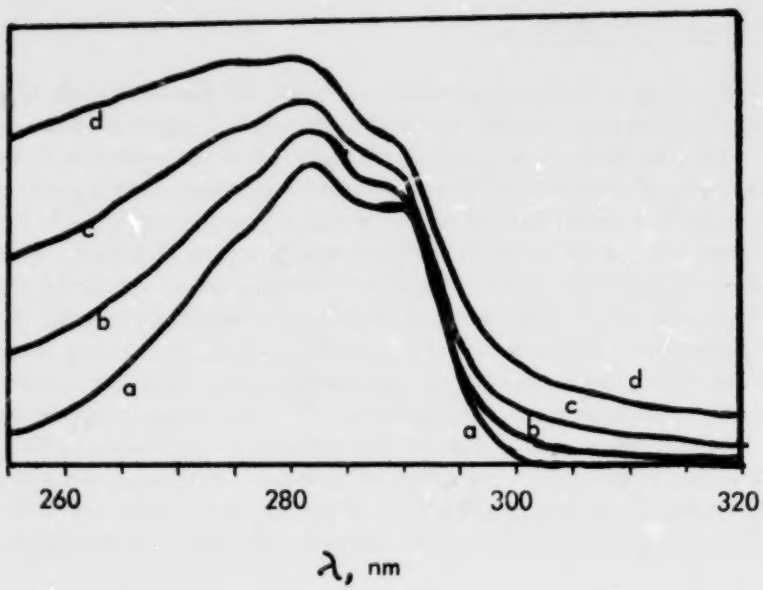


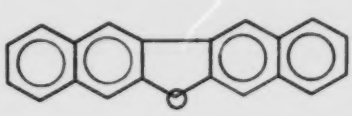
FIGURE 3 Photolysis of 2,4-D methyl ester in water

a initial spectrum
b after 120 min photolysis period
c after 240 min photolysis period
d after 360 min photolysis period

The photodecomposition products from Sevin have been rather problematic in the literature. Crosby and coworkers[30] reported that 1-naphthol and several cholinesterase inhibitors were photoproducts. We have ruled out 1-naphthol as a photoproduct under our conditions, but have not identified any primary photoproducts.

Furthermore, we have shown that photolysis of 1-naphthol in water or methanol does not give the photoproducts observed for Sevin. In addition, we have shown that 1-methoxynaphthalene is not a photoproduct from the photolysis of Sevin in methanol. The isolable product distribution is highly dependent on the length of time following the photolysis that workup is initiated. Available analytical information (UV and NMR) indicates that the complex mixture is characteristic of that expected for subsequent oxidation. When photolyzed to about 60% conversion in 50% EtOH: H_2O, the Sevin is converted to at least 5 different products three of which are exceedingly polar (cannot be moved on silica tlc). Several of these fluoresce and the long wavelength fluorescence and absorption of one of the non-polar products (compound A) implies a system of extended conjugation. Compound A has emission bands at 415, 440 and 458 cm. A high resolution mass spectrum of this compound is relatively clean with a molecular ion of m/e equal to 268.0870, which

corresponds to a molecular formula $C_{20}H_{12}O$. Two major peaks in the IR at 3005 cm^{-1} and 1200 cm^{-1} correspond to that published for:



We have examined the effect of the presence and absence of O_2 on the photolysis in H_2O. When photolyzed for 1 hour (1.5×10^{-4} M Sevin; 254 nm irradiation) in air saturated water, only a small fraction of Sevin remains. The aqueous solution is light brown. Sevin appears to be the only ether extractable material remaining. A weak fluorescence band at 425 nm was noted. The Rayleigh scatter (apparent by inspection of the solution) implies an insoluble suspension in the aqueous solution. Addition of K_2CO_3 clears the suspension immediately implying a phenolic-type functional group. When photolyzed after N_2 purging in water, the solution remains

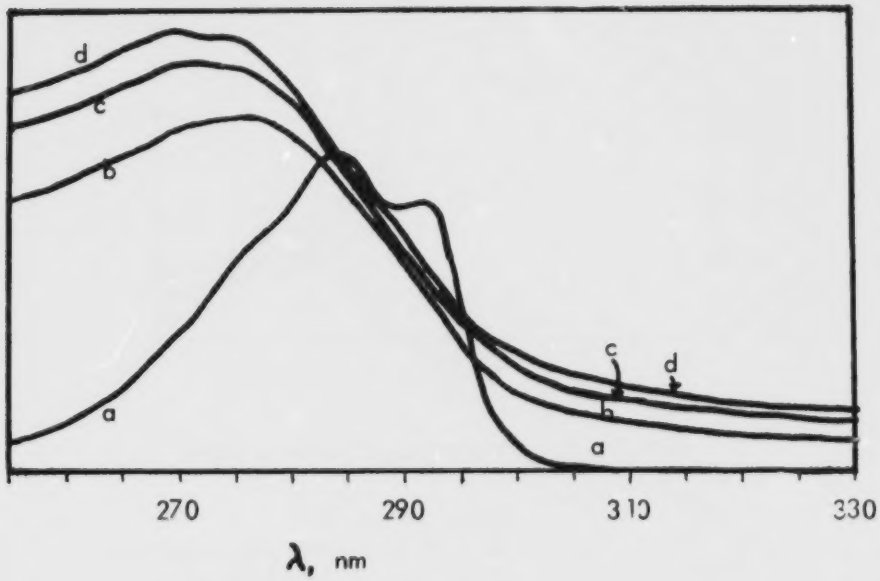


FIGURE 4 Photolysis of 2,4-D methyl ester with anionic detergent

a initial spectrum
b after 120 min photolysis period
c after 180 min photolysis period
d after 240 min photolysis period

FIGURE 5 Photolysis of Sevin in water

a initial spectrum
b after 60 min photolysis period
c after 120 min photolysis period
d after 300 min photolysis period

FIGURE 6 Photolysis of Sevin with cationic detergent

a initial spectrum
b after 15 min photolysis period
c after 30 min photolysis period
d after 60 min photolysis period

FIGURE 7 Photolysis of Sevin with anionic detergent

a initial spectrum
b after 75 min photolysis period
c after 180 min photolysis period
d after 390 min photolysis period

colorless but a similar suspension forms. The dispersion does not clear up upon addition of K_2CO_3 and air. Photolysis of this solution, however, does clear up the dispersion, and the solution becomes light brown. The UV spectra is identical to the solution originally containing oxygen. We conclude that the intial Sevin photochemistry is not sensitive to oxygen but that the secondary photochemistry is. Singlet oxygen produced by the decomposition of potassium perchromate (K_2CrO_3) in water[31] does not produce any changes in the absorption spectrum of Sevin.

The photodecomposition of parathion has been reported to result in the formation of paraoxon,[32] p-nitrophenol[33] and other unidentified products.[32] In our studies neither p-nitrophenol nor paraoxon was detected in quantities greater than 2% of the workup mixture at conversions of approximately 50%. Two volatile (gas chromatography) photoproducts remain unidentified.

SOIL STUDIES

The soils used in our studies are typical arable types differing widely in pH level, organic content, nature of exchangeable cations present, etc. Pertinent characteristics are given in Table 5. The surfactants studied were of the anionic (SDS) and cationic (HDTBr) types. The moisture content of the soils was varied and can be categorized as follows:

(1) Dry: soil that was dried with no additional water added.
(2) Saturated: dried soil to which a quantity of water was added to fill the "pore space". This quantity depends on the individual soil and amounts to roughly 1 milliliter per gram soil. It has been found that when detergents are co-applied, an additional quantity of water is required to give the visual appearance of saturation. The additional quantity is probably used in hydration of the surfactant head group.
(3) Wet-dry soils to which quantities of water (up to 4 ml) were added to form slurries.

Table 5. SOIL CHARACTERISTICS

Type	Name	Slurry pH	%Carbon	Bulk Density	%Pore Space
I	Etowah	4.4	0.13	1.70	35.8
II	Holston	6.3	0.60	1.90	28.3
III	Conasauga Siltloam	7.6	2.79	1.57	40.8
IV	Holston-sub soil	4.9	—	1.80	32.0

The general procedure (referred to as "standard conditions") involves preparation of a uniform soil surface by spreading an aqueous slurry containing 1 gram soil on a 10x15 cm surface (Figure 8) and allowing the surface to dry completely. This produces an average soil thickness of ca. 0.003 cm. The pesticide (5 mg) and, in certain case, detergent (100 mg) are dissolved in 5 ml acetone or methanol and spread uniformly on the thin soil film. The solvents are evaporated completely. This corresponds to a coverage of 2.9 lbs. pesticide per acre and 58 lbs. surfactant per acre. For those experiments involving water-saturated or wet soils, an appropriate amount of water is uniformly added to surface. The vessel is then sealed and photolyzed. An identical vessel is simultaneously prepared and stored in the dark for an equivalent time period. The samples are photolyzed on a custom-built glass tray with cooling water circulating on the under side to avoid evaporative losses and to maintain the initial moisture content. The trays are tightly covered with Pyrex glass on top and are placed about 14 cm under a horizontal water-cooled Pyrex-jacketted medium pressure Hg arc (450 W) as shown in Figure 8. The radiant density is reasonably uniform over the entire surface.

The output of the lamp, as constructed and filtered by Pyrex, provides radiation with approximately the following photo flux on the plate surface.

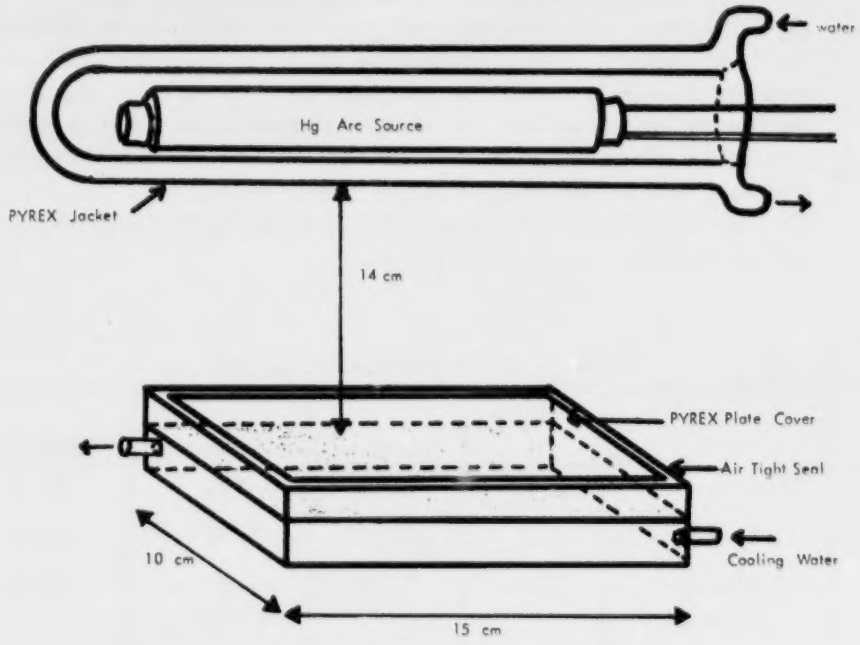


Figure 8 Apparatus for photolysis on soil surfaces

λ(nm)	total incident light (Einsteins-sec^{-1})
297	0.58×10^{-7}
303	1.4×10^{-7}
313	4.4×10^{-7}
334	1.1×10^{-7}

Longer wavelength light is not absorbed by the pesticides used and shorter wavelength light is totally filtered by the Pyrex. As determined by the extinction coefficients, the quantity applied is such that only a fraction of the incident intensity is absorbed. Consequently, it is expected that the extent of photolysis should fall off exponentially with time. Experiments at various time intervals have confirmed this expectation (see Figure 9). The bulk of our experiments were run at exposure times of 18-150 hrs, but in order to facilitate comparison, the results are reported in terms of the time required for 50% photodecomposition. Very crude

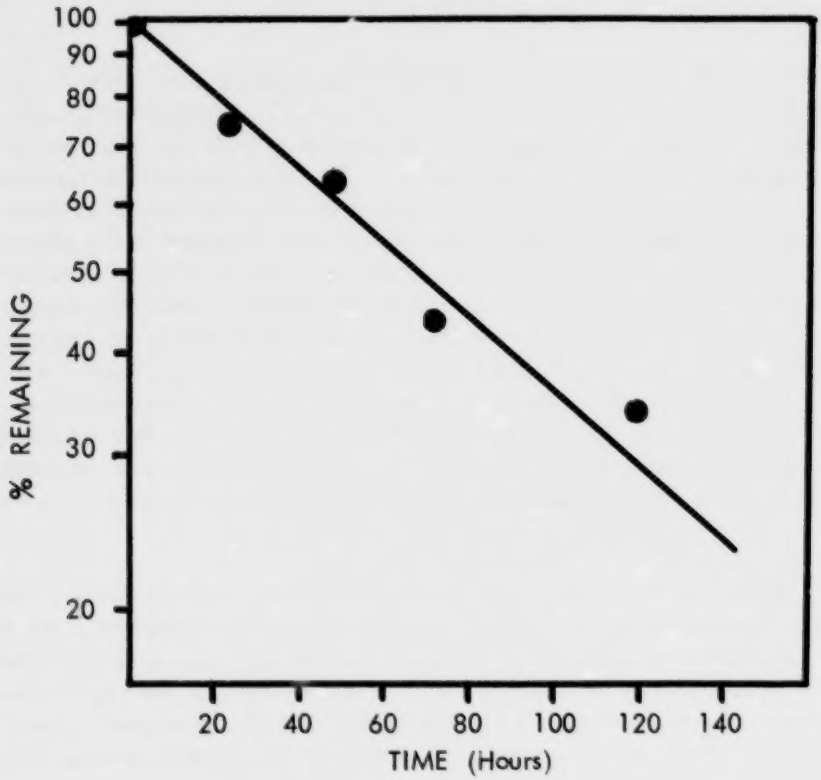


Figure 9 Photodecomposition of 2,4-D on soil I (dry) as a function of time

quantum yields can be calculated by assuming that extinction data in solution is applicable to soil surfaces (see experimental section).

The photolysis of 2,4-D was carried out on the acid rather than the various esters actually used as pesticides because it was found that hydrolysis of the ester to the acid occurred very rapidly on the soils studied. Reproducibility of the 2,4-D experiments was a problem, particularly with the experiments carried out on "wet" soils. Our early experiments under such conditions exhibited substantially faster decomposition rates. The amount of water was not as carefully controlled in those experiments and exceeded 4 ml. The results presented in Table 6 are the most recent and "best values. The photodecomposition rates vary by a factor of seven over the conditions studied. No meaningful trends were observed, and the most important conclusion to be derived is that the photolysis of 2,4-D on soils is very slow and inefficient. In the most favorable case, a crude quantum yield of 0.003 has been estimated. This is approximately 30 times lower than the efficiency observed in aqueous solution. As noted above, excessive quantities of water added to the soil may enhance the photodecomposition rates substantially but this effect is likely due to solubilization into the aqueous phase in which the photochemistry is significantly more efficient (particularly in the presence of detergents).

Similar studies using the pesticide Sevin are presented in Table 7. In the absence of detergents, the photochemistry is very slow; with increasing water content, it is literally inert. The presence of detergents retards the "dry" soil photochemistry somewhat; however, as moisture is added the decomposition becomes very facile. The observation that detergents catalyze the dark hydrolysis of Sevin to 1-naphthol and the observation that 1-naphthol can be detected in the photochemical experiments only when short irradiation periods are used, lead to the conclusion that the non-photochemical hydrolysis catalyzed by detergents is primarily responsible for the dramatic effects. Again very crude quantum yields can be calculated for these experiments. A value of 0.0003 for the experiment on "dry" soil I with no detergent is so obtained. In aqueous solution, the value is approximately 30 times greater. A fourth type of soil (designated soil IV) was used in a few experiments. It was employed as a replacement for soil I, the supply of which was exhausted. Both are acidic soils (pH$\sim$4), and the behavior of IV was found to be similar to that of soil I.

In Table 8 are listed the results for a similar study with parathion. The acidic soil IV was used exclusively as a replacement for soil I. For parathion, the rate of photodecomposition was not found to correlate with soil type or soil moisture content. The effect of added detergent was also insignificant except for the slight retardation (approximately a factor of two) observed using the cationic detergent. Again the "quantum yields" of photolysis were found to be very low on soil surfaces (but closer to those in solution).

Graphical representations of the data presented in Tables 6-8 are given in Figures 10-12. The calculated "quantum yields" are included in these figures. As

indicated previously (section on photolysis rates-Part A), it is useful to calculate actual photolysis half-lives for sunlight conditions. Using the "quantum yields" as obtained above and extinction coefficient data from aqueous solution, these half-lives for sunlight conditions have been calculated and are included in the appendix. A summary of the pertinent data is given in Table 9.

Each of the studies reported above for the decomposition of 2,4-D, Sevin, and parathion on soil surfaces was carried out under a standard set of conditions in order to facilitate comparison. The conditions chosen were environmentally realistic ones

Table 6. EFFECTS OF SOIL TYPES, DETERGENTS AND SOIL WATER CONTENT ON THE TIME REQUIRED FOR 50% PHOTODECOMPOSITION of 2,4-D

Soil	Detergent	Water Content	Time Required for 50% Photodecomposition (hours)
I	none	dry	86
I	HDTBr	dry	93
I	SDS	dry	71
II	none	dry	99(282)[a]
II	HDTBr	dry	88
II	SDS	dry	115
III	none	dry	160
III	HDTBr	dry	102(221)[a]
III	SDS	dry	242
I	none	satd.	99(202)[a]
I	HDTBr	satd.	154
I	SDS	satd.	130
II	none	satd.	105(282)[a]
II	HDTBr	satd.	173
II	SDS	satd.	149
III	none	satd.	187
III	HDTBr	satd.	149(220)[a]
III	SDS	satd.	69
I	none	wet	80(101)[a]
I	HDTBr	wet	205
I	SDS	wet	121
II	none	wet	141(234)[a]
II	HDTBr	wet	285
II	SDS	wet	101
III	none	wet	149(168)[a]
III	HDTBr	wet	121(149)[a]
III	SDS	wet	42

a) Half-life of dark control for those cases in which it is significant.

Table 7. EFFECTS OF SOIL TYPES, DETERGENTS AND SOIL WATER CONTENT ON THE TIME REQUIRED FOR 50% PHOTODECOMPOSITION OF SEVIN

Soil	Detergent	Water Content	Time Required for 50% Photodecomposition (hrs)
I	none	dry	97
I	none	satd.	529
I	none	wet	538
II	none	dry	251
II	none	satd.	688
II	none	wet	458
III	none	dry	105
III	none	satd.	(286)[a]
III	none	wet	538
I	HDTBr	dry	251
I	HDTBr	satd.	159
I	HDTBr	wet	(34)[b]
IV	HDTBr	wet	(35)[c]
II	HDTBr	dry	358
II	HDTBr	satd.	(201)[a]
II	HDTBr	wet	(20-60)[d]
III	HDTBr	dry	251
III	HDTBr	satd.	(41)[b]
III	HDTBr	wet	(10-50)[d]
I	SDS	dry	274
I	SDS	satd.	251
I	SDS	wet	(30)[b]
IV	SDS	wet	(64)[c]
II	SDS	dry	251
II	SDS	wet	(29)[d]
III	SDS	dry	251
III	SDS	satd.	224
III	SDS	wet	(24)[d]

a) The dark control in this case gave identical results; hence the slow decomposition might not be photochemical in nature

b) The dark control showed large conversion of Sevin to α-naphthol; no α-naphthol was found in the photochemical experiment

c) At short reaction times, both the dark control and the photochemical experiment showed extensive conversion of Sevin to α-naphthol

d) Variable results were obtained; the dark controls indicated extensive conversion to α-naphthol; α-naphthol was detected in the photochemical experiments only for short irradiation times.

Table 8. EFFECTS OF SOIL TYPES, DETERGENTS AND SOIL WATER CONTENT ON THE TIME REQUIRED FOR 50% PHOTODECOMPOSITION OF PARATHION

Soil	Detergent	Water Content	Time Required for 50% Photodecomposition (hours)
IV	none	dry	52
IV	none	satd.	34
IV	none	wet	47
II	none	dry	61
II	none	satd.	31
II	none	wet	44
III	none	dry	70
III	none	satd.	36
II	none	wet	36
IV	HDTBr	dry	134
IV	HDTBr	satd.	191
IV	HDTBr	wet	51
II	HDTBr	dry	106
II	HDTBr	satd.	93
II	HDTBr	wet	61
III	HDTBr	dry	90
III	HDTBr	satd.	65
III	HDTBr	wet	102
IV	SDS	dry	43
IV	SDS	satd.	70
IV	SDS	wet	34
II	SDS	dry	38
II	SDS	satd.	72
II	SDS	wet	32
III	SDS	dry	109
III	SDS	satd.	61
III	SDS	wet	36

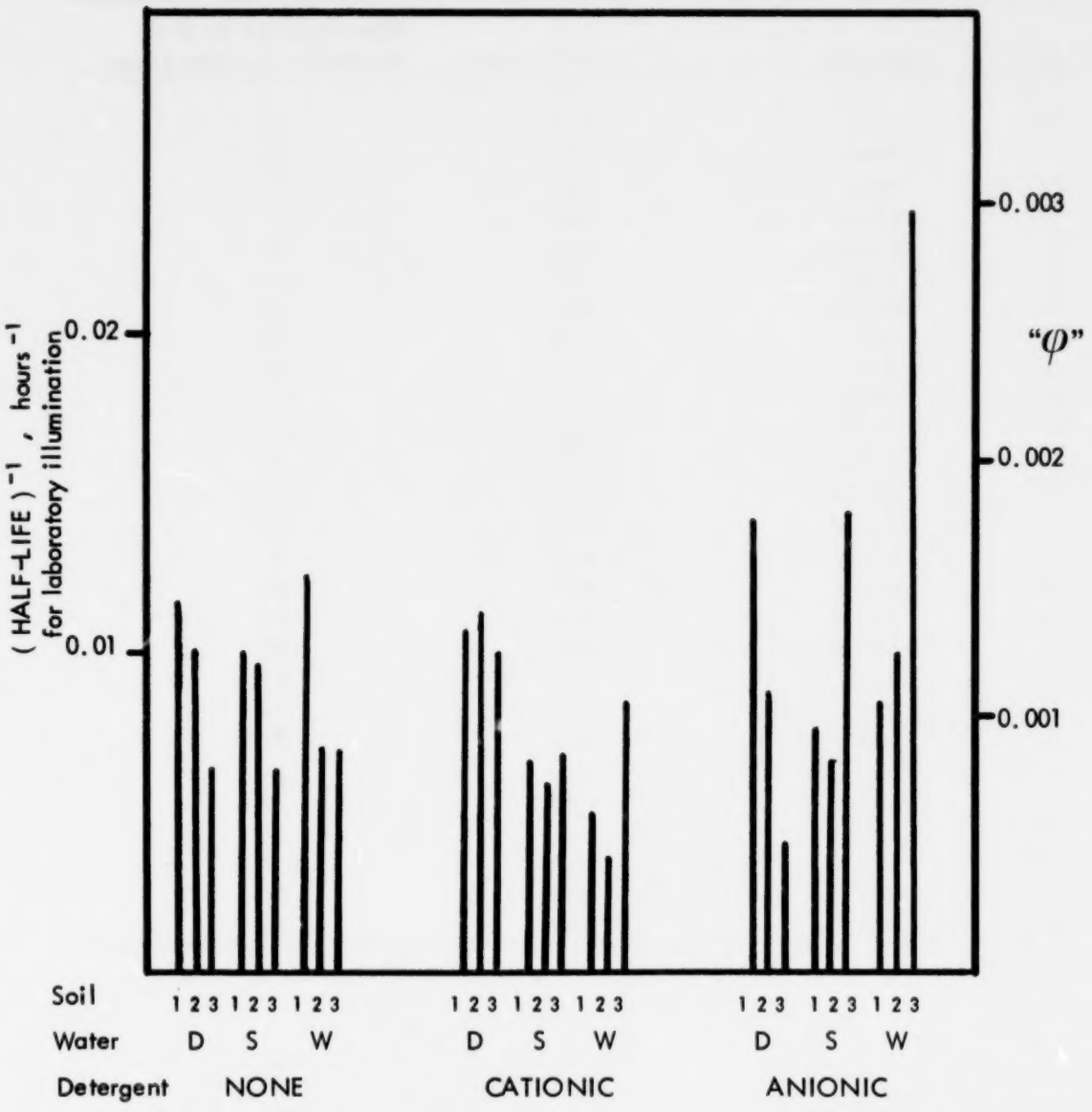


FIGURE 10 Graphical representation of the extent of photocomposition of 2,4-D on soils
(D, S, and W correspond to dry, saturated and wet respectively)

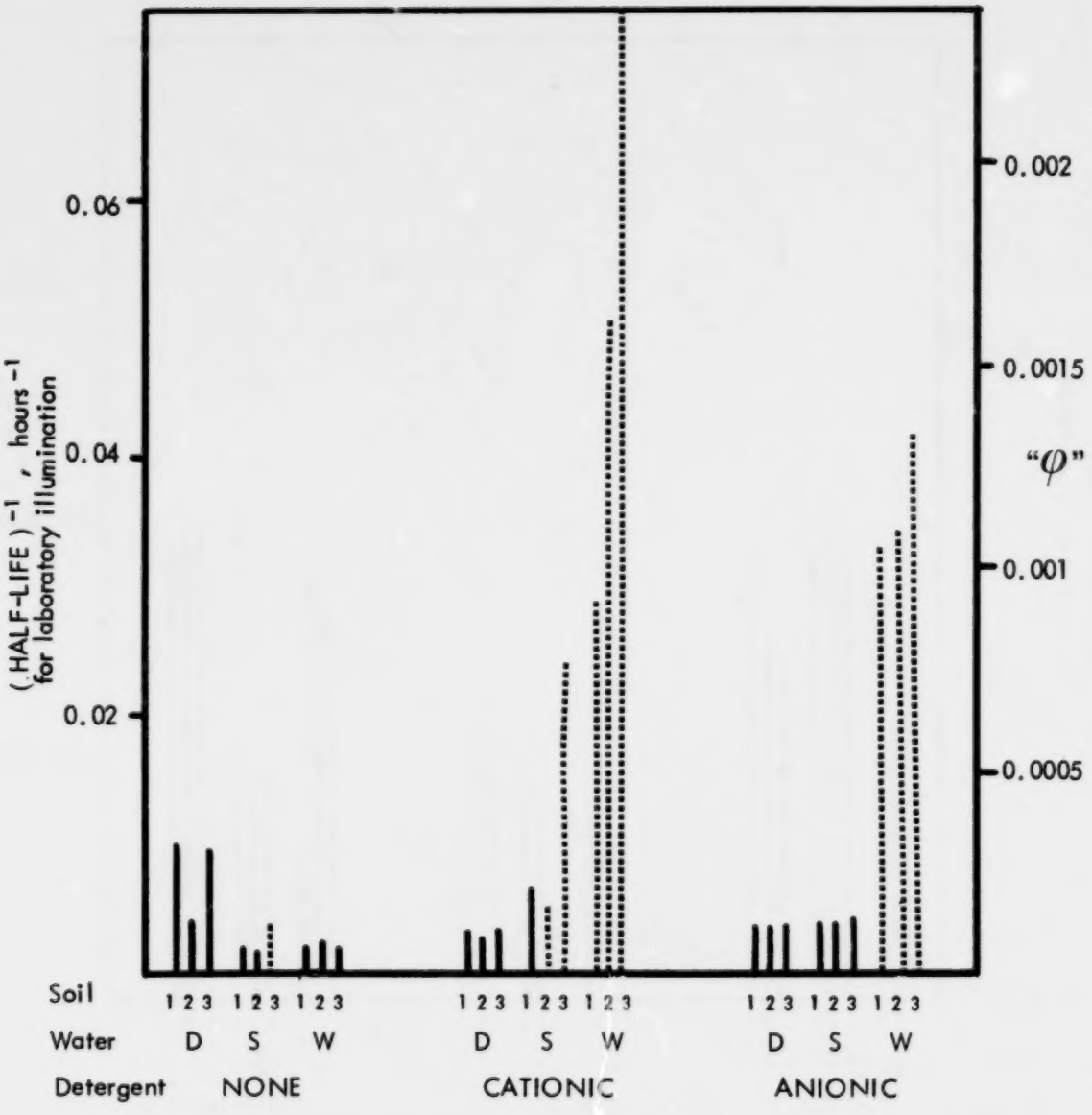


FIGURE 11 Graphical Representation of the Extent of Photodecomposition of Sevin on Soils
(D, S, and W correspond to dry, saturated and wet respectively; see text for details of experiments graphed with broken lines)

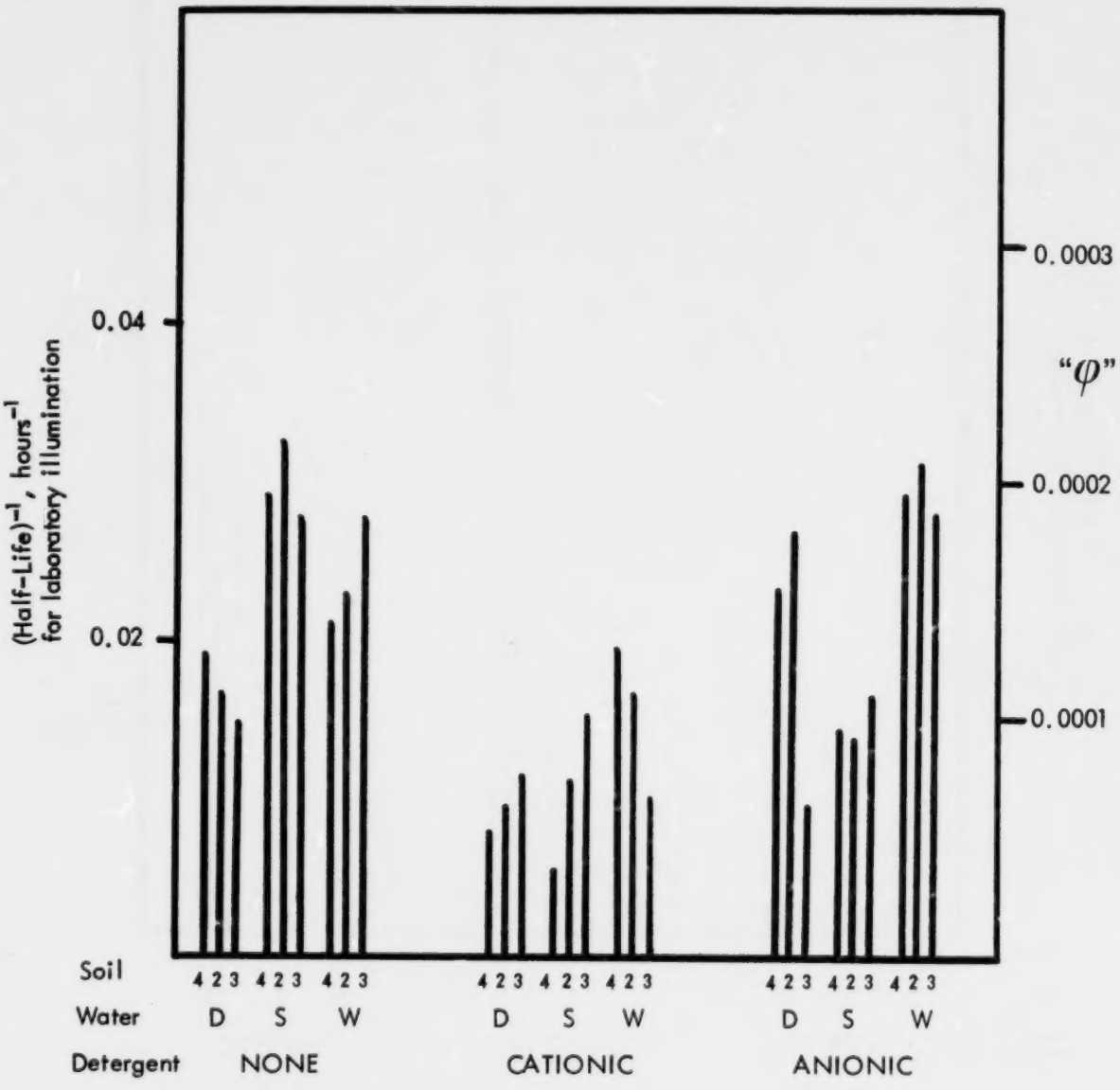


FIGURE 12 Graphical Representation of the Extent of Photodecomposition of Parathion on Soils
(D, S, and W correspond to dry, saturated and wet respectively)

Table 9. CALCULATED PHOTOLYSIS HALF-LIVES FOR 2,4-D SEVIN AND PARATHION ON SOIL SURFACES IRRADIATED BY SUNLIGHT

Pesticide	"Quantum Yield"[a]	Half-Life (days)[b]
2,4-D acid	0.003	1250.
	0.001	3750.
	0.0005	7500.
Sevin	0.002	51.
	0.0003	380.
	0.00005	2500.
Parathion	0.00022	8.5
	0.0001	18.
	0.000037	50.

a) The "quantum yields" represent the extreme values and a typical value for the various conditions studied as taken from Figures 10, 11, and 12.

b) Average clear days during midsummer at 40°N latitude. See appendix for complete data.

but were nonetheless fixed. In order to ascertain whether the specific quantities of materials chosen for the "standard" conditions gave representative results, these parameters were varied using the parathion-soil III system. The following factors were systematically varied:

standard values	parameter varied
1 g soil	3 g soil
5 mg pesticide	1 mg pesticide
100 mg detergent	20 mg detergent

The results of this study are presented in Table 10. Inspection of these results shows that the only variable that affects the results is the quantity of soil used. As the amount of soil is increased the decomposition rate decreases slightly in all cases. This small effect is readily attributable to screening of the pesticide from the available light. This suggest that the already very inefficient photochemistry on soil surfaces diminishes rapidly with penetration into the soil. It should be noted that studies

employing the greater quantity of soil still results in a very thin layer of soil (ca. 0.01 cm). Allied to our studies of pesticide photochemistry on soil surfaces was a study of the absorption and emission spectroscopy of adsorbed species on surfaces. We were interested in determining whether adsorption on soils results in shifts in the UV absorption spectra. Such studies are best carried out using a double monochromator UV spectrophotometer (due to the enormous background absorption of soils). In principle, however, such information can be obtained by taking the excitation spectrum of a species that fluoresces. We have readily observed such spectra with polycondensed aromatics such as anthracene on glass surfaces, but such species have highly structured spectra. Any subtle changes due to adsorption either do not exist or are not discernible by this approach.

Table 10. EFFECTS OF PARAMETER VARIATIONS ON THE PHOTODECOMPOSITION OF PARATHION ON SOIL III

Soil	Parathion	Water Content	Detergent	Time Required for 50% Photodecomposition (hrs)
1 g	1 mg	dry		75
1 g	1 mg	satd.		31
1 g [a]	5 mg	dry		70
1 g [a]	5 mg	satd.		36
1 g	5 mg	wet		36
3 g	5 mg	dry		93
3 g	5 mg	satd.		45
1 g	1 mg	dry	100 mg cationic	90
1 g	1 mg	satd.	100 mg cationic	63
1 g	5 mg	dry	20 mg cationic	93
1 g	5 mg	satd.	20 mg cationic	65
1 g [a]	5 mg	dry	100 mg cationic	90
1 g [a]	5 mg	satd.	100 mg cationic	65
1 g [a]	5 mg	wet	100 mg cationic	102
3 g	5 mg	dry	100 mg cationic	149
3 g	5 mg	satd.	100 mg cationic	65
1 g	1 mg	dry	100 mg anionic	86
1 g	1 mg	satd.	100 mg anionic	31
1 g	5 mg	dry	20 mg anionic	57
1 g	5 mg	satd.	20 mg anionic	32
1 g [a]	5 mg	dry	100 mg anionic	109
1 g [a]	5 mg	satd.	100 mg anionic	61
1 g [a]	5 mg	wet	100 mg anionic	36
3 g	5 mg	dry	100 mg anionic	158
3 g	5 mg	satd.	100 mg anionic	85

a) Refers to standard conditions.

One of the important conclusions we have reached regarding photochemistry on soils is that it is very slow and inefficient. A reasonable explanation for this observation is that the photoexcited pesticide is quenched (possibly through energy transfer) by pigments in the soil. We have attempted to gain information on this point by examining the fluorescence of various species deposited on soil surfaces and comparing them with the corresponding results on glass surfaces. If the hypothesis is correct, both the fluorescence intensity and the fluorescence lifetime should be lowered for samples on soils (if competitive absorption by the soils is responsible only the intensity would decrease). The experiments have been carried out in the following manner. Glass slides (with and without soil films) are sprayed (misted) with dilute ethereal solutions of the fluorescer. The soil treated and untreated slides are placed side by side to ensure uniform application. Front surface emission spectra are recorded after each spray (numerous sprays are required before fluorescence is detectable under any conditions). We have found that on plain glass surfaces the fluorescence becomes readily detectable. Under identical conditions on the soil slides no fluorescence is detected (it is totally quenched). The fluorescence lifetimes for the glass slide experiments are readily determined and are generally comparable to solution values. The extraordinarily weak emission from the "soil" experiments gives a decay so short it can not be resolved from the short lamp decay. Of course, the weak decay observed could simply be residual light scatter if there were no fluorescence at all. See Figure 13 for typical results using α-naphthol. These findings support our conclusions concerning the inefficient soil photochemistry.

Product Studies on Soils

Our analysis conditions have shown that no low molecular weight, volatile products (detectable by gas chromatography) are produced from the photolysis of any pesticide we have photolyzed on soils. Controls of expected photoproducts and/or hydrolysis products indicate that we can recover these quantitatively from the soil samples.

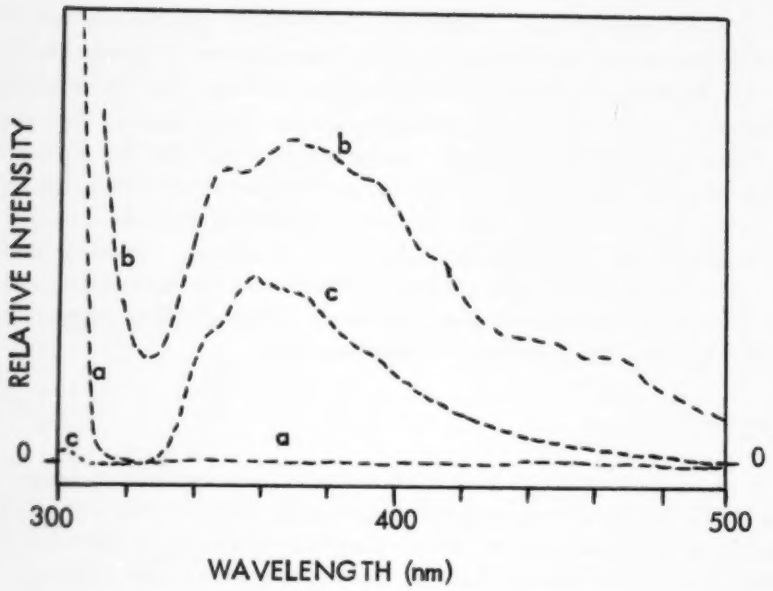


Figure 13. Fluorescence Spectra of 1-Naphthol

a on soil III
b on glass
c in solution (ether)

SECTION V

EXPERIMENTAL

MATERIALS

2,4-Dichlorophenoxyacetic acid, 4-chlorophenoxyacetic acid, and 2-chlorophenoxyacetic acid were recrystallized twice from chloroform-hexane mixtures. The corresponding methyl and butoxyethyl esters were prepared by acid catalyzed esterification in benzene. The esters were purified by vacuum distillation and recrystallization when possible. Authentic samples of chlorohydroxyphenoxyacetic acids for use as gas chromatography standards were obtained from R. G. Zepp. Sevin was prepared by reacting 1-naphthol with methyl isocyanate in benzene containing 2% pyridine for 5 hours at 80°C in a bomb. Although recrystallization (from toluene and from ether/hexane/ gave a sharp melting material (mp. 141.8-142.9°C) it was not chromatographically (TLC) homogeneous. Following column chromatography (silica gel eluted with methylene chloride) and recrystallization from methylene chloride, white crystalline material that was homogeneous by TLC was obtained (m.p. 141.0-141.5°C). N-methyl-1-hydroxy-2-naphthamide and methyl 4-hydroxy-1-naphthoate obtained from R.G.Zepp were purified by silica-gel column chromatography (chloroform and 1:3 ether/benzene, respectively, as eluents). Parathion was prepared by heating p-nitrophenol, sodium carbonate and diethyl chlorothiophosphate in acetone. After appropriate washings, the parathion was distilled under vacuum. Paraoxon was prepared both by bromine oxidation of parathion and by treatment with sodium p-nitrophenoxide and chlorodiethylphosphate. Hexadecyltrimethylammonium bromide was prepared by heating (50°C) trimethylamine and freshly distilled 1-bromo-hexadecane in ethanol for 5 hours under a dry-ice acetone condenser. The material was recrystallized four times from ether/ethanol. Commercially available material was found to be unsatisfactory (even after several recrystallization) in certain cases. Sodium dodecyl sulfate (Pfaltz and Bauer) was recrystallized from 95% ethanol taking care not to overheat (<55°C). Brij-35 (Baker) was used as received and was chromatographed on silica gel (hexane-chloroform) with no apparent improvement. The water used in these studies was triply-distilled first from dichromate, then from alkaline permanganate and finally from an all-glass still. The soil samples were purified and characterized in the laboratories of Professor H. F. Perkins (Agronomy Department, University of Georgia). All other materials used were reagent grade quality.

EQUIPMENT

Ultraviolet-visible spectra were recorded using a Cary 15 spectrophotometer or a Gilford Model 222 spectrophotometer. Fluorescence spectra were measured with a Hitachi-Perkin Elmer MPF-3A spectrofluorimeter. Fluorescent lifetimes were measured by the single-photon-counting technique using the Ortec Model 9500 instrument schematically illustrated in Figure 14. Gas chromatographic analyses were made using a Varian 2740 dual flame ionization instrument. High-pressure liquid chromatography was first carried out with a Waters liquid chromatograph equipped with UV and refractive index detectors. The bulk of the experiments reported, however, were done using a Varian 8500 gradient elution instrument equipped with variable wavelength UV detector. Routine nmr spectra were taken on Varian T-60 or HA-100 instruments and routine infrared spectra were taken on a Perkin-Elmer 621 spectrophotometer.

Soil surface photolyses were carried out using the setup illustrated in Figure 8. The sample holder was cooled by running water underneath the glass surface containing the soil sample. A 2-mm-thick optical quality Pyrex plate was sealed with masking tape atop the vessel after the application was made. Irradiation was provided by a 450 W Hanovia medium pressure Hg arc cooled by a standard Pyrex immersion well, which also provided two 1.5-mm thicknesses of Pyrex glass to filter the light.

Certain (as indicated in the text) solution phase quantum yields were measured on an optical bench with a thermostatted cell compartment accommodating standard 1-cm quartz cuvettes. Light of 290 nm was provided by a 200-W super pressure Hg arc (Bausch and Lomb power supply and lamp housing) and was isolated through a high intensity Bausch and Lomb grating monochromator. The light intensity was fairly constant and was monitored routinely using ferrioxalate actinometry (ϕ= 1.24).[34] Other solution phase quantum yields were measured on a standard photochemical merry-go-round apparatus. Light was provided by a 450-W Hanovia medium pressure mercury arc inside a Pyrex immersion well. The immersion well was cooled by circulating an aqueous solution containing 1.5×10^{-3} M K_2CrO_4 and 3% K_2CO_3. This filter solution in combination with the Pyrex walls effectively isolates the 313 nm line of the Hg arc. Visible light is filtered out through four Corning 7-54 filters mounted in a metal sheath that surrounds the immersion well. Sample tubes on the moving outer turn-table of the merry-go-round are irradiated equivalently and simultaneously. The light intensity with this setup was found to be very constant and was monitored routinely be ferrioxalate[34] or valerophenone[35] actinometry.

Preparative photochemical experiments were carried out in sealed vessels surrounding the Pyrex immersion well containing a Hanovia 450-W medium-pressure Hg arc. Vessels of several shapes and sizes accommodating solution volumes from 75 to 1200 ml were used. In each case, the capability to purege the solution with nitrogen and maintain an oxygen-free atmosphere was available.

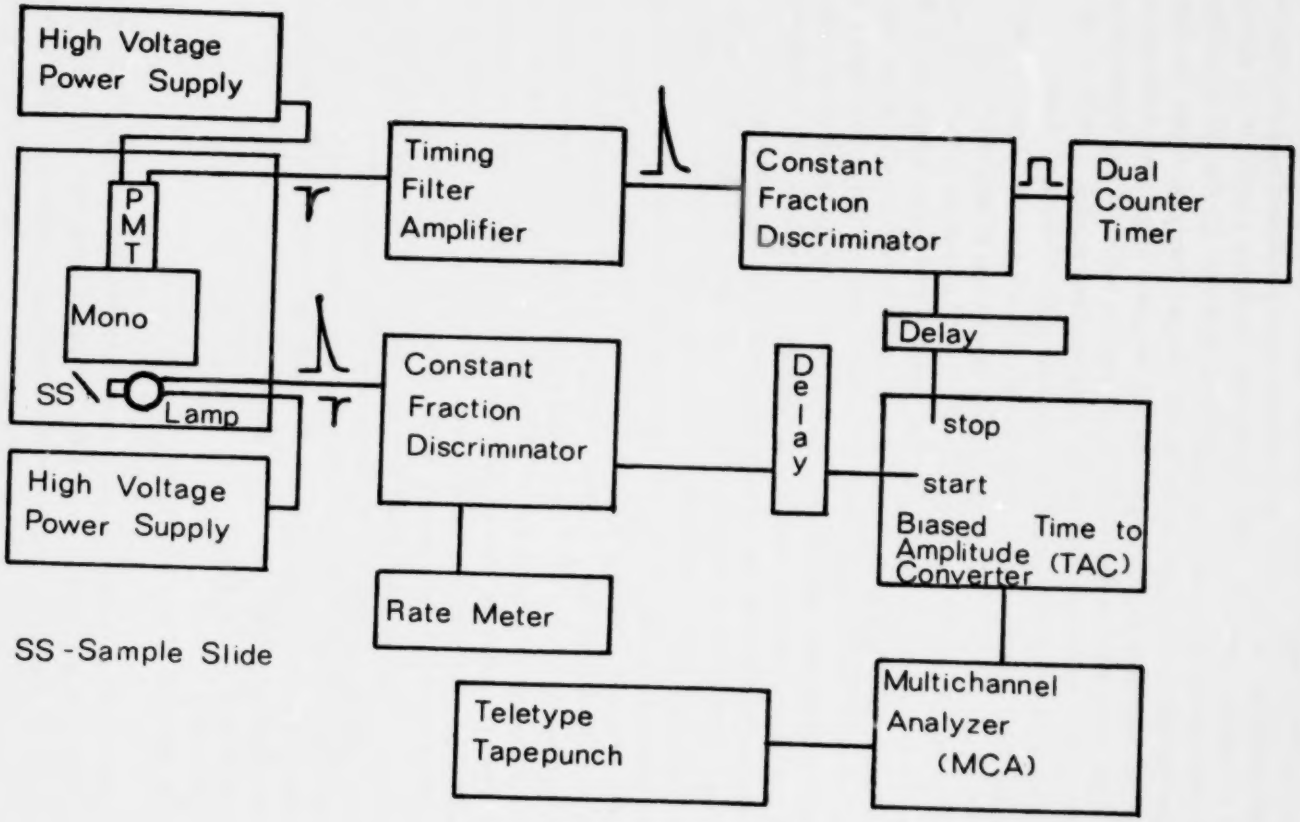


Figure 14. Schematic Diagram for the High Resolution time Resolved Emission Spectrometer

"QUANTUM YIELD" DETERMINATIONS ON SOIL SURFACES

Determinations of approximate "quantum yields" were based on the assumption that the pesticide absorbed the fraction of available light predicted by extinction coefficient values in aqueous solution. This assumption would be invalid if (1) distribution of the pesticide over the surface were not reasonably uniform, (2) the soil particles masked access to the light, (3) pigments in the soil competitively absorbed the light or (4) adsorption of the pesticide on to the soil surface resulted in spectral shifts of the pesticide. We have no evidence that any of these factors exists to any appreciable extent for the thin soil surfaces and techniques used in these studies. There is, of course, no question that factor (2) would be dominant with thicker soil layers. Solution extinction coefficients, (ϵ), expressed in units of ℓ-mole^{-1}-cm^{-1}, can be converted into values (ϵ'; $\epsilon' = 1000\,\epsilon$) applicable to surfaces of any depth and, therefore, the fraction of incident absorbed ($1-10^{-\epsilon' c'}$) by a given quantity of pesticide per centimeter can be caluclated. For the standard conditions employed in these experiments (5 mg pesticide), the number of moles-cm^{-2} (c') of 2,4-D, Sevin and parathion were 1.5×10^{-7}, 1.9×10^{-7} and 1.1×10^{-7}, respectively. The light source employed in these experiments was not monochromatic but rather consisted of lines at 297, 303, 313 and 334 nm (longer wavelength lines are inconsequential and shorter wavelength lines are absorbed by the glass filteres before reaching the surface). The intensities of these lines (Einsteins-sec^{-1} -150 cm^{-2}) incident to the surface were calculated from manufacturer's specifications and were attenuated by calculating the fraction of each absorbed by the three glass filters in between the lamp and the soil surface. The values so obtained (listed in the text) were assumed to be rather crude. In order to test the validity of these values, an aqueous solution containing 1.0×10^{-4} M p-nitroanisole and 1.0×10^{-2} M NaOH was photolyzed in the compartment. It is known that the quantum efficiency for production of p-nitrophenoxide is 0.0052. The fraction of light absorbed by this solution was similarly calculated. The solution was photolyzed for 6 minutes and analyzed for p-nitrophenoxide. The intensity of the lamp calculated by this "actinometer" was within 20% of that predicted by the above calculations. Thus, this approach was deemed satisfactory for obtaining sufficiently accurate values consistent with the nature of the experiment. The stability of the light source over long periods of time was very good. This was monitored by periodically repeating one of the highly reproducible soil experiments. Small corrections were made to adjust the experimental half-lives to a consistent intensity value throughout the course of this work.

QUANTUM YIELDS FOR SOLUTION STUDIES

The photolysis equipment used for these determinations has been described above. The solutions were prepared so that the concentrations were near 1×10^{-4} M (this was done so that studies in detergent-free aqueous solutions could be done under comparable conditions). The fraction of light absorbed was measured at the exciting wavelength and the solutions were worked-up and analyzed in a manner identical to that described for the preparative experiments. Because the small amounts of materials

used were subjected to extensive extraction and workup procedures, the error in these experiments is larger than typical for a quantum yield determination. Consequently the values obtained are reported to only one significant figure and are likely to have error limits of ± 30% although this was not statistically determined.

DETERMINATION OF EXTINCTION COEFFICIENTS

Extinction coefficients were determined in a conventional manner by preparing solutions of accurately known concentrations. In each case, however the materials were sparingly soluble and the accuracy of values obtained diminishes as the wavelength increases. Ordinarily a higher concentration solution could be prepared to obtain such values, but solubility limitations preclude this in water. In the cases of detergent solutions, the solubility of a solute can be enhanced markedly; however, this frequently requires days of stirring to gain appreciable increases in solubility. Because the pesticides were found to undergo micelle catalyzed hydrolysis reactions in certain cases, no attempt was made to make quantitative measurements in more concentrated solutions.

In each case the reference solution contained the appropriate detergent.

FLUORESCENCE MEASUREMENTS ON SURFACES

Glass slides were cut to fit diagonally into the sample holder of the fluorescence spectrometer and the time-resolved emission spectrometer. This configuration allows for front-surface excitation and for observation of front-surface emission. Slides were dipped into an aqueous slurry of the soil (soil III) and allowed to oven dry. The thickness of the soil sample appeared to be comparable to those used in the photochemical studies. A clean glass slide was placed adjacent to a soil-coated one for each experiment. An ether solution of the fluorescing species was prepared and placed in a pump spray bottle. (Commercial hair spray bottles that produce a fine mist were found to be satisfactory for this purpose.(The solution was sprayed at the two slides taking care to make the application uniform. The slides were placed in the fluorescence spectrometer and removed to respray until a desirable level of fluorescence was detected. In each case, the soil-coated and the soil-free slide received the same spray treatment. After the spectra were recorded for both slides, they were placed in the time-resolved emission spectrometer and emission decay curves were taken. The results obtained for 1-naphthol are presented in Figure 13 and are typical. Similar results were obtained for N-methylquinolinium iodide, naphthalene and Sevin. With naphthalene, volatilization was a serious problem. The intensity of the emission on the glass plate steadily decreased while taking the spectra, although the results obtained were qualitatively similar. For N-methylquinolinium, iodide solubility problems precluded the use of ether. Methanol was used although this was not entirely satisfactory as evaporation required lengthier times and "puddling" effects occurred on the surface.

SOIL SURFACE PHOTOCHEMICAL STUDIES

The general procedure for applying the soil, pesticide, detergent and water along with a description of the apparatus have been discussed in the Results section. It should be noted that this procedure evolved out of numerous attempts to prepare the surfaces in a uniform and reproducible fashion. Attempts to apply aqueous solutions containing the pesticide and detergent were found to be totally unsatisfactory for numerous reasons including the unwieldy volume of water necessary, the excessive evaporation times necessary, loss of the pesticide through volatilization and hydrolysis, lack of uniform water content after evaporation and obvious (visually) disturbances of the uniformity of the soil surface. The final procedure used eliminated each of these problems. For each experiment, two identical surfaces were prepared. One was kept in the dark for the same period of time as the sample photolyzed. The photolysis procedure has been described previously in the experimental section. The surfaces were "worked-up" and analyzed as described below. A standard solution containing the exact quantity of pesticide applied was prepared in each case. The dark control and the photolyzed sample were compared relative to the standard. Except as noted, the concentration of pesticide in the dark control was identical (±5%) with the standard solution.

For experiments involving 2,4-D acid, the soil samples were extracted with four 50-ml portions of 1 N $NaHCO_3$. The extract was filtered through Whatman No. 1 filter paper and 25 cm^3 of concentrated HCl was added. The acidified extract was extracted with six 50-ml portions of ether. After evaporation of the ther, the residue was esterified by taking 2 ml of methanolic BF_3, which was heated at 70°C for 1 hour. Then 5 ml of saturated NaCl was added and the solution was extracted five times with 50-ml portions of benzene. The benzene was evaporated and the residue dissolved in 5 ml of acetone for analysis by gas chromatography. For experiments with HDTBr, 2 ml of 1 M KI was added after the initial bicarbonate extraction. The precipitate of hexadecyltrimethylammonium iodide was filtered off. Otherwise the procedure was identical. For experiments involving SDS, 1 M $BaCl_2$ was added to precipitate the detergent. The solutions were analyzed by gas chromatography.

For experiments involving Sevin, the soils were extracted with four 50-ml portions of acetone and filtered. The acetone was evaporated and the residue diluted to 5 ml with ethanol. This solution was analyzed by liquid chromatography (C-18 reversed phase column with 10% ethanol-water). When HDTBr was present, the soils were extracted with methanol, potassium iodide was added to precipitate the detergent and the precipitate washed with ether which was evaporated. Finally, the residue was diluted to volume with ethanol and analyzed by liquid chromatography. For experiments involving SDS, the detergent was precipitated with $BaCl_2$.

For experiments with parathion, the extraction was identical to that for Sevin. The residue was diluted to volume with acetone and analyzed by gas chromatography. For all of the soil experiments, known or expected hydrolysis and photolysis products of the pesticides were subjected to the workup procedures and analysis. In all cases,

the absence of these and other volatile products (gas chromatography) were observed in the photolysis mixture.

PRODUCT ANALYSIS OF SOLUTION PHOTOLYSES

For 2,4-D methyl ester, Sevin and parathion, preparative scale photolyses were carried out in order to identify photoproducts. These were photolyzed in water and in aqueous solutions of HDTBr and SDS. In addition, Sevin was photolyzed in methanol and aqueous ethanol. The photochemical equipment used for the photolyses are described elsewhere in the experimental section.

Studies involving the methyl ester of 2,4-D were carried out with initial concentrations of 4×10^{-4} M. The 1-liter solutions were not deoxygenated. The photolysis times were varied from 10 minutes to 2 hours. The solutions were extracted with methylene chloride, which was dried and evaporated *in vacuo*. The residue was diluted to volume with acetone and analyzed by gas chromatography. For the runs with HDTBr, a ten-fold excess of cation exchange resin was added to the aqueous solution after photolysis. The resin was filtered and extracted with ether. The detergent free aqueous solution was extracted with ether. The ether extracts were combined, dried and evaporated *in vacuo*. The residue was diluted to volume with acetone and analyzed by gas chromatography. For the runs with SDS, $BaCl_2$ was added to precipitate the detergent. The precipitate was washed and solution extracted with ether. Workup was otherwise similar.

In aqueous solution, photolysis for 10 minutes netted 17% loss of 2,4-D methyl ester with tiny amounts (<2% each) of seven photoproducts. Longer photolysis times (20 and 40 minutes) increased the yields of these products but not proportional to the loss of 2,4-D. A 2-hour photolysis resulted in virtually total loss of 2,4-D but also loss of the initial photoproducts. The retention times of 2,4-dichlorophenol, methyl *p*-chlorophenoxyacetate, methyl *o*-chlorophenoxyacetate and methyl 2-chloro-4-hydroxyphenoxyacetate corresponded to four of the photoproducts. Preparative thick-layer and gas chromatography were used to attempt to isolate the photoproducts. This was unsuccessful.

The photolysis carried out in solution containing HDTBr (20 minutes) was analyzed and a complex chromatogram resulted. This was later shown to be related to small amounts of impurities in the detergent. The only obvious feature of the chromatogram was an absence of the peak related to 2,4-dichlorophenol and a major peak presumably due to methyl *p*-chlorophenoxyacetate.

The photolysis carried out in SDS solution (10 minutes) gave no peaks that could be related to known photoproducts. Again, the chromatogram was obscured by detergent impurities.

The photolysis of parathion was studied in aqueous solution and in aqueous solution containing HDTBr (2.8×10^{-3} M) and SDS (1.0×10^{-2} M). In each case, an

800-ml solution containing 5×10^{-5}M parathion was photolyzed for approximately 3 hours (2 hours for the solution containing SDS). The solutions were extracted with ether (after precipitating the detergents with either KI or $BaCl_2$), which was dried and evaporated in vacuo. The residue were diluted to volume with acetone and analyzed by gas chromatography. In each case, 200 ml of an identical solution was kept in the dark and worked up at the same time as the photolysis mixture. The dark controls revealed small losses of parathion for the non-detergent and SDS solutions. Approximately 42% of the parathion was lost in the dark control for the cationic detergent solution. In the photolyzed solutions, 48% of the parathion in the aqueous solution, 83% in the HDTBr solution and 92% in the SDS solution. In none of the cases was p-nitrophenol or paraoxon present in quantities over 2-3%. Two unidentified peaks were present in the gas chromatograph.

Numerous attempts were made to photolyze aqueous solutions of Sevin (with and without detergents) in order to determine its elusive photochemical fate. Aqueous solutions (350 ml) containing 3.5×10^{-4} M Sevin (and 1×10^{-2} M HDTBr or 5×10^{-2} M SDS in certain cases) were photolyzed in "doughnut" shaped vessels fitted around a Pyrex immersion well. Photolysis times were varied in half-hour increments from 30 min to 4 hours. After photolysis, 1 g KI was added to the HDTBr solutions and the precipitate was filtered after stirring. For the SDS solutions, 3 g $BaCl_2$ was added. In all cases, the solutions were then extracted with ether (along with the precipitates). The ether was evaporated and the residue diluted to volume with ethanol. The solutions were analyzed by liquid chromatography (10% ethanol-water on a reversed phase column). The following results were obtained:

Photolysis time (hr)	% Photolyzed		
	Water	1×10^{-2}M HDTBr	5×10^{-2}M SDS
0.5	12.	29.	-
1.0	17.	37.	-
1.5	25.	65.	29
2.0	28.	74.	-
2.5	32.	0	-
3.0	34.	-	-
4.0	-	-	39

For each of these runs, no α-naphthol was detected. Judging by the color of the solutions a photoproduct more soluble in water than in ether (or other organic solvents) was present. UV spectra of the aqueous solution after extraction clearly showed the instability of this product as the broad structureless spectra (λ_{max} 350 mm) changed with time. An unidentified peak in the LC had the same retention volume as N-methyl-1-hydroxyl-2-naphthamide. None of methyl 4-hydroxy-1-naphthoate was detected by LC. Thin layer chromatography ($CHCl_3$ on silica) also ruled out the latter, which

exhibited a bright blue fluorescence (R_f = 0.6) not observed in the TLC of the reaction mixture. If any N-methyl-1-hydroxy-2-naphthamide were present, it could not be detected by thin layer chromatography (R_f = 0.5). Other than Sevin only a spot at the origin showed up by TLC.

Other liquid chromatography conditions ($C_{10}NH_2$ column, THF: heptane (1:8) or silica gel column and 30% mixture of 1% 2-propanol in hexane with 70% 10% 2-propanol in methylene chloride) revealed nothing new. Several wavelengths were used for detection.

The initial concentration of Sevin in aqueous solution was varied from 1.0 x 10^{-4} M to 5.67 x 10^{-4} M with no unusual effects. Again no α-naphthol was detected.

The concentration of HDTBr was varied from 0 to 1 x 10^{-3} M to 5 x 10^{-3} M to 1 x 10^{-2} M. The maximum photolysis was observed at 5 x 10^{-3} M but the amount was not significantly greater than that of 1 x 10^{-2} M.

In order to gain more information on the elusive photoproducts, Sevin was photolyzed in methanol and in aqueous ethanol. Photolysis of Sevin in methanol followed by evaporation of methanol gave a residue which was analyzed by nmr and TLC. No α-naphthol or 1-methoxynaphthalene were present. A singlet observed at δ 3.9 ppm, however, was indicative of an aryl methoxyl group. Photolyses in aqueous-ethanol and several studies involving photolysis of Sevin in water using a 254-nm lamp on aerated and deoxygenated solutions were carried out, the salient features of which were described in the results section.

SECTION VI

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SECTION VII

GLOSSARY

Brij-35: A non-ionic detergent (see text for structure)

CMC: Critical micelle concentration-the concentration at which micelles form

Detergent: A term used interchangeably with surfactant to designate an amphilic molecule (one with a large distinct non-polar and a distinct polar or ionic region)

2,4-D: 2,4-Dichlorophenoxyacetic acid (see text for structure)

Einstein: 6.023×10^{23} photons of light

Extinction coefficient: A quantitative measure of the light absorbing characteristics of a compound; expressed in units of liters-mole^{-1} cm^{-1}

HDTBr: Hexadecyltrimethylammonium bromide, a cationic detergent (see text for structure); also abbreviated CTAB

λ: Wavelength (expressed in nanometers)

Micelle: An aggregate of several ($\sim$100) detergent molecules in solution

nm: Nanometers (10^{-9} meters)

Φ: Quantum yield

ϕdis: Quantum yield for disappearance of a compound undergoing photodecomposition

Quantum efficiency: see quantum yield

Quantum yield: The ratio of molecules undergoing a particular light-reduced process relative to the number of photons of light absorbed

Sevin: N-methyl-1-naphthylcarbamate, often refered to as Carbaryl (see text for structure)

SDS: Sodium dodecyl sulfate, an anionic detergent (see text for structure)

Solar spectral irradiance: The distribution of sunlight reaching the earth's surface in terms of intensity as a function of wavelength

Surfactant: see Detergent

UV: Ultraviolet region of the electromagnetic spectrum

SECTION VIII

APPENDIX

The rates of photodecomposition of 2,4-D, Sevin and parathion under typical solar conditions have been caluclated and are presented in this appendix. Values for extinction coefficients and quantum yields were taken from this study. The calculations were carried out by Dr. Richard G. Zepp of the Environmental Protection Agency, Athens, Georgia. For a brief discussion of the approach see the section on Photolysis Rates; for a detailed discussion see reference 26.

System: 2,4-D methyl ester in aqueous solution

```
XENOBIOTIC NAME: 2,4-D,METHYL ESTER
WATER IDENTIFICATION: PURE
QUANTUM YIELD:          0.06000
INITIAL DEPTH:          0.00100
DEPTH INCREMENT:       10.00000
FINAL DEPTH:            5.00000
REFRACTIVE INDEX:       1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.2360E+03
   300.00  *      0.00280     * 0.7870E+02
   302.50  *      0.00260     * 0.5250E+02
   305.00  *      0.00250     * 0.3940E+02
   307.50  *      0.00240     * 0.3940E+02
   310.00  *      0.00230     * 0.2620E+02
   312.50  *      0.00220     * 0.2620E+02
   315.00  *      0.00210     * 0.1310E+02
   317.50  *      0.00200     * 0.1310E+02
   320.00  *      0.00190     * 0.0000E+00
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: 2,4-D,METHYL ESTER
WATER IDENTIFICATION: PURE LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.798E-10	0.241E+07
		10.00	6.25	17.60	0.207E-09	0.931E+06
		20.00	7.12	16.73	0.621E-08	0.310E+05
		30.00	7.99	15.85	0.320E-07	0.601E+04
		40.00	8.91	14.94	0.135E-06	0.143E+04
		50.00	9.93	13.92	0.278E-06	0.692E+03
		60.00	11.75	12.10	0.374E-06	0.515E+03
	MIDDAY	60.09	11.92	11.92	0.375E-06	0.514E+03

AVG RATE DURING DALITE(SEC**-1) 0.179E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.854E-02
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.811E+2
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.798E-10	0.241E+07
		10.00	5.76	18.22	0.207E-09	0.931E+06
		20.00	6.65	17.33	0.621E-08	0.310E+05
		30.00	7.52	16.46	0.320E-07	0.601E+04
		40.00	8.39	15.59	0.135E-06	0.143E+04
		50.00	9.28	14.70	0.278E-06	0.692E+03
		60.00	10.24	13.74	0.374E-06	0.515E+03
		70.00	11.84	12.14	0.449E-06	0.429E+03
	MIDDAY	70.09	11.99	11.99	0.449E-06	0.429E+03

AVG RATE DURING DALITE(SEC**-1) 0.212E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.111E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.625E+2
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.798E-10	0.241E+07
		10.00	7.18	16.20	0.207E-09	0.931E+06
		20.00	8.16	15.22	0.621E-08	0.310E+05
		30.00	9.30	14.08	0.320E-07	0.601E+04
		40.00	11.52	11.86	0.135E-06	0.143E+04
	MIDDAY	40.06	11.69	11.69	0.136E-06	0.142E+04

AVG RATE DURING DALITE(SEC**-1) 0.665E-07
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.263E-02
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.264E+3
NEAR SURFACE

```
40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                5.00    7.79   16.38   0.798E-10   0.241E+07
               10.00    8.31   15.85   0.207E-09   0.931E+06
               20.00    9.52   14.64   0.621E-08   0.310E+05
    MIDDAY     29.86   12.08   12.08   0.317E-07   0.608E+04

               AVG RATE DURING DALITE(SEC**-1)  0.182E-07
               RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.638E-03
               HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.109E+4
               NEAR SURFACE
```

System: 2,4-D methyl ester in aqueous solution with cationic surfactant

```
XENOBIOTIC NAME: 2,4-D,METHYL ESTER
WATER IDENTIFICATION: .01M CTAB
QUANTUM YIELD:        0.10000
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.4990E+03
   300.00  *      0.00280     * 0.1970E+03
   302.50  *      0.00260     * 0.7870E+02
   305.00  *      0.00250     * 0.3940E+02
   307.50  *      0.00240     * 0.2620E+02
   310.00  *      0.00230     * 0.1310E+02
   312.50  *      0.00220     * 0.0000E+00
   315.00  *      0.00210     * 0.0000E+00
   317.50  *      0.00200     * 0.0000E+00
   320.00  *      0.00190     * 0.0000E+00
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: 2,4-D,METHYL ESTER
WATER IDENTIFICATION: .01M CTAB LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.517E-12	0.372E+09
		10.00	6.25	17.60	0.165E-12	0.117E+10
		20.00	7.12	16.73	0.167E-10	0.115E+08
		30.00	7.99	15.85	0.723E-09	0.266E+06
		40.00	8.91	14.94	0.822E-08	0.234E+05
		50.00	9.93	13.92	0.304E-07	0.633E+04
		60.00	11.75	12.10	0.476E-07	0.405E+04
	MIDDAY	60.09	11.92	11.92	0.477E-07	0.404E+04
		AVG RATE DURING DALITE(SEC**-1) 0.202E-07				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.965E-03				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.718E+3				
		NEAR SURFACE				
40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.517E-12	0.372E+09
		10.00	5.76	18.22	0.165E-12	0.117E+10
		20.00	6.65	17.33	0.167E-10	0.115E+08
		30.00	7.52	16.46	0.723E-09	0.266E+06
		40.00	8.39	15.59	0.822E-08	0.234E+05
		50.00	9.28	14.70	0.304E-07	0.633E+04
		60.00	10.24	13.74	0.476E-07	0.405E+04
		70.00	11.84	12.14	0.642E-07	0.300E+04
	MIDDAY	70.09	11.99	11.99	0.643E-07	0.300E+04
		AVG RATE DURING DALITE(SEC**-1) 0.266E-07				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.139E-02				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) [illegible]3				
		NEAR SURFACE				
40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.517E-12	0.372E+09
		10.00	7.18	16.20	0.165E-12	0.117E+10
		20.00	8.16	15.22	0.167E-10	0.115E+08
		30.00	9.30	14.08	0.723E-09	0.266E+06
		40.00	11.52	11.86	0.822E-08	0.234E+05
	MIDDAY	40.06	11.69	11.69	0.834E-08	0.231E+05
		AVG RATE DURING DALITE([illegible]**-1) 0.373E-08				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.148E-03				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.470E+4				
		NEAR SURFACE				

```
40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                5.00    7.79   16.38   0.517E-12   0.372E+09
               10.00    8.31   15.85   0.165E-12   0.117E+10
               20.00    9.52   14.64   0.167E-10   0.115E+08
    MIDDAY     29.86   12.08   12.08   0.714E-09   0.270E+06

               AVG RATE DURING DALITE(SEC**-1)  0.379E-09
               RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.133E-04
               HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.522E+5
               NEAR SURFACE
```

System: 2,4-D methyl ester in aqueous solution with anionic surfactant

```
XENOBIOTIC NAME: 2,4-D,METHYL ESTER
WATER IDENTIFICATION: .05M SDS
QUANTUM YIELD:        0.10000
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.4070E+03
   300.00  *      0.00280     * 0.1710E+03
   302.50  *      0.00260     * 0.7870E+02
   305.00  *      0.00250     * 0.5250E+02
   307.50  *      0.00240     * 0.3940E+02
   310.00  *      0.00230     * 0.2640E+02
   312.50  *      0.00220     * 0.2640E+02
   315.00  *      0.00210     * 0.2640E+02
   317.50  *      0.00200     * 0.1310E+02
   320.00  *      0.00190     * 0.1310E+02
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: 2,4-D,METHYL ESTER
WATER IDENTIFICATION: .05M SDS LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.412E-09	0.467E+06
		10.00	6.25	17.60	0.125E-08	0.155E+06
		20.00	7.12	16.73	0.279E-07	0.690E+04
		30.00	7.99	15.85	0.122E-06	0.158E+04
		40.00	8.91	14.94	0.445E-06	0.432E+03
		50.00	9.93	13.92	0.846E-06	0.228E+03
		60.00	11.75	12.10	0.111E-05	0.173E+03
	MIDDAY	60.09	11.92	11.92	0.111E-05	0.173E+03

AVG RATE DURING DALITE(SEC**-1) 0.546E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.261E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.266E+2
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.412E-09	0.467E+06
		10.00	5.76	18.22	0.125E-08	0.155E+06
		20.00	6.65	17.33	0.279E-07	0.690E+04
		30.00	7.52	16.46	0.122E-06	0.158E+04
		40.00	8.39	15.59	0.445E-06	0.432E+03
		50.00	9.28	14.70	0.846E-06	0.228E+03
		60.00	10.24	13.74	0.111E-05	0.173E+03
		70.00	11.84	12.14	0.131E-05	0.147E+03
	MIDDAY	70.09	11.99	11.99	0.131E-05	0.147E+03

AVG RATE DURING DALITE(SEC**-1) 0.637E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.333E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.208E+2
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.412E-09	0.467E+06
		10.00	7.18	16.20	0.125E-08	0.155E+06
		20.00	8.16	15.22	0.279E-07	0.690E+04
		30.00	9.30	14.08	0.122E-06	0.158E+04
		40.00	11.52	11.86	0.445E-06	0.432E+03
	MIDDAY	40.06	11.69	11.69	0.448E-06	0.430E+03

AVG RATE DURING DALITE(SEC**-1) 0.224E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.887E-02
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.782E+2
NEAR SURFACE

```
40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                5.00    7.79   16.38   0.412E-09   0.467E+06
               10.00    8.31   15.85   0.125E-08   0.155E+06
               20.00    9.52   14.64   0.279E-07   0.690E+04
    MIDDAY     29.86   12.08   12.08   0.120E-06   0.160E+04

               AVG RATE DURING DAYLITE(SEC**-1)  0.703E-07
               RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.246E-02
               HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.281E+3
               NEAR SURFACE
```

System: 2,4-D acid on soil surfaces. The data here are calculated for conditions producing a "quantum yield" of 0.001. See complete data for 2,4-D -soil experiments to obtain actual "quantum yields" for specific conditions.

```
XENOBIOTIC NAME: 2,4-D,ACID
WATER IDENTIFICATION: SOIL SURFACE
QUANTUM YIELD:        0.00100
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.2360E+03
   300.00  *      0.00280     * 0.7870E+02
   302.50  *      0.00260     * 0.5250E+02
   305.00  *      0.00250     * 0.3940E+02
   307.50  *      0.00240     * 0.3940E+02
   310.00  *      0.00230     * 0.2620E+02
   312.50  *      0.00220     * 0.2620E+02
   315.00  *      0.00210     * 0.1310E+02
   317.50  *      0.00200     * 0.1310E+02
   320.00  *      0.00190     * 0.0000E+00
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: 2,4-D,ACID
WATER IDENTIFICATION: SOIL SURFACE LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.133E-11	0.145E+09
		10.00	6.25	17.60	0.345E-11	0.559E+08
		20.00	7.12	16.73	0.103E-09	0.186E+07
		30.00	7.99	15.85	0.533E-09	0.361E+06
		40.00	8.91	14.94	0.225E-08	0.856E+05
		50.00	9.93	13.92	0.464E-08	0.415E+05
		60.00	11.75	12.10	0.623E-08	0.309E+05
	MIDDAY	60.09	11.92	11.92	0.624E-08	0.308E+05

AVG RATE DURING DALITE(SEC**-1) 0.298E-08
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.142E-03
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.487E+4
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.133E-11	0.145E+09
		10.00	5.76	18.22	0.345E-11	0.559E+08
		20.00	6.65	17.33	0.103E-09	0.186E+07
		30.00	7.52	16.46	0.533E-09	0.361E+06
		40.00	8.39	15.59	0.225E-08	0.856E+05
		50.00	9.28	14.70	0.464E-08	0.415E+05
		60.00	10.24	13.74	0.623E-08	0.309E+05
		70.00	11.84	12.14	0.748E-08	0.258E+05
	MIDDAY	70.09	11.99	11.99	0.748E-08	0.257E+05

AVG RATE DURING DALITE(SEC**-1) 0.354E-08
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.185E-03
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.375E+4
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.133E-11	0.145E+09
		10.00	7.18	16.20	0.345E-11	0.559E+08
		20.00	8.16	15.22	0.103E-09	0.186E+07
		30.00	9.30	14.08	0.533E-09	0.361E+06
		40.00	11.52	11.86	0.225E-08	0.856E+05
	MIDDAY	40.06	11.69	11.69	0.226E-08	0.851E+05

AVG RATE DURING DALITE(SEC**-1) 0.111E-08
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.436E-04
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.158E+5
NEAR SURFACE

```
 40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                 5.00    7.79   16.38   0.133E-11   0.145E+09
                10.00    8.31   15.85   0.345E-11   0.559E+08
                20.00    9.52   14.64   0.103E-09   0.186E+07
      MIDDAY    29.86   12.08   12.08   0.528E-09   0.365E+06

                AVG RATE DURING DALITE(SEC**-1)  0.303E-09
                RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.106E-04
                HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.652E+5
                NEAR SURFACE
```

System: Sevin in aqueous solution

```
XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: PURE WATER
QUANTUM YIELD:        0.01000
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.1410E+04
   300.00  *      0.00280     * 0.9300E+03
   302.50  *      0.00260     * 0.7370E+03
   305.00  *      0.00250     * 0.5290E+03
   307.50  *      0.00240     * 0.4090E+03
   310.00  *      0.00230     * 0.3510E+03
   312.50  *      0.00220     * 0.3780E+03
   315.00  *      0.00210     * 0.2580E+03
   317.50  *      0.00200     * 0.2360E+03
   320.00  *      0.00190     * 0.1120E+03
   323.10  *      0.00180     * 0.5790E+02
   330.00  *      0.00152     * 0.1380E+02
   340.00  *      0.00122     * 0.0000E+00
   350.00  *      0.00100     * 0.0000E+00
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: PURE WATER LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.111E-07	0.174E+05
		10.00	6.25	17.60	0.277E-07	0.695E+04
		20.00	7.12	16.73	0.121E-06	0.160E+04
		30.00	7.99	15.85	0.333E-06	0.578E+03
		40.00	8.91	14.94	0.898E-06	0.214E+03
		50.00	9.93	13.92	0.154E-05	0.125E+03
		60.00	11.75	12.10	0.198E-05	0.975E+02
	MIDDAY	60.09	11.92	11.92	0.198E-05	0.973E+02

AVG RATE DURING DALITE(SEC**-1) 0.102E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.485E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.143E+2
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.111E-07	0.174E+05
		10.00	5.76	18.22	0.277E-07	0.695E+04
		20.00	6.65	17.33	0.121E-06	0.160E+04
		30.00	7.52	16.46	0.333E-06	0.578E+03
		40.00	8.39	15.59	0.898E-06	0.214E+03
		50.00	9.28	14.70	0.154E-05	0.125E+03
		60.00	10.24	13.74	0.198E-05	0.975E+02
		70.00	11.84	12.14	0.229E-05	0.841E+02
	MIDDAY	70.09	11.99	11.99	0.229E-05	0.840E+02

AVG RATE DURING DALITE(SEC**-1) 0.117E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.609E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.114E+2
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.111E-07	0.174E+05
		10.00	7.18	16.20	0.277E-07	0.695E+04
		20.00	8.16	15.22	0.121E-06	0.160E+04
		30.00	9.30	14.08	0.333E-06	0.578E+03
		40.00	11.52	11.86	0.898E-06	0.214E+03
	MIDDAY	40.06	11.69	11.69	0.902E-06	0.213E+03

AVG RATE DURING DALITE(SEC**-1) 0.485E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.192E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.361E+2
NEAR SURFACE

```
40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                5.00    7.79   16.38   0.111E-07   0.174E+05
               10.00    8.31   15.85   0.277E-07   0.695E+04
               20.00    9.52   14.64   0.121E-06   0.160E+04
     MIDDAY    29.86   12.08   12.08   0.330E-06   0.583E+03

               AVG RATE DURING DAYLITE(SEC**-1)  0.206E-06
               RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.728E-02
               HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.952E+2
               NEAR SURFACE
```

System: Sevin in aqueous solution with cationic surfactant

```
XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: .01M CTAB
QUANTUM YIELD:          0.03000
INITIAL DEPTH:          0.00100
DEPTH INCREMENT:       10.00000
FINAL DEPTH:            5.00000
REFRACTIVE INDEX:       1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.2450E+04
   300.00  *      0.00280     * 0.1730E+04
   302.50  *      0.00260     * 0.1320E+04
   305.00  *      0.00250     * 0.1040E+04
   307.50  *      0.00240     * 0.8030E+03
   310.00  *      0.00230     * 0.6830E+03
   312.50  *      0.00220     * 0.6220E+03
   315.00  *      0.00210     * 0.5290E+03
   317.50  *      0.00200     * 0.4400E+03
   320.00  *      0.00190     * 0.3320E+03
   323.10  *      0.00180     * 0.2470E+03
   330.00  *      0.00152     * 0.5790E+02
   340.00  *      0.00122     * 0.1160E+02
   350.00  *      0.00100     * 0.5800E+01
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: .01M CTAB LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.232E-06	0.831E+03
		10.00	6.25	17.60	0.553E-06	0.348E+03
		20.00	7.12	16.73	0.184E-05	0.104E+03
		30.00	7.99	15.85	0.424E-05	0.454E+02
		40.00	8.91	14.94	0.939E-05	0.205E+02
		50.00	9.93	13.92	0.147E-04	0.131E+02
		60.00	11.75	12.10	0.184E-04	0.104E+02
	MIDDAY	60.09	11.92	11.92	0.184E-04	0.104E+02

AVG RATE DURING DALITE(SEC**-1) 0.995E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.475E+00
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.146E+1
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.232E-06	0.831E+03
		10.00	5.76	18.22	0.553E-06	0.348E+03
		20.00	6.65	17.33	0.184E-05	0.104E+03
		30.00	7.52	16.46	0.424E-05	0.454E+02
		40.00	8.39	15.59	0.939E-05	0.205E+02
		50.00	9.28	14.70	0.147E-04	0.131E+02
		60.00	10.24	13.74	0.184E-04	0.104E+02
		70.00	11.84	12.14	0.210E-04	0.915E+01
	MIDDAY	70.09	11.99	11.99	0.211E-04	0.914E+01

AVG RATE DURING DALITE(SEC**-1) 0.112E-04
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.586E+00
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.118E+1
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.232E-06	0.831E+03
		10.00	7.18	16.20	0.553E-06	0.348E+03
		20.00	8.15	15.22	0.184E-05	0.104E+03
		30.00	9.30	14.06	0.424E-05	0.454E+02
		40.00	11.52	11.86	0.939E-05	0.205E+02
	MIDDAY	40.06	11.69	11.69	0.941E-05	0.204E+02

AVG RATE DURING DALITE(SEC**-1) 0.536E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.212E+00
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.327E+1
NEAR SURFACE

```
 40.00 WINTER    0.00    7.21   16.95  0.000E+00  0.000E+00
                 5.00    7.79   16.38  0.232E-06  0.831E+03
                10.00    8.31   15.85  0.553E-06  0.348E+03
                20.00    9.52   14.64  0.184E-05  0.104E+03
     MIDDAY     29.86   12.08   12.08  0.421E-05  0.458E+02

                AVG RATE DURING DALITE(SEC**-1)  0.275E-05
                RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.966E-01
                HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.718E+1
                NEAR SURFACE
```

System: Sevin in aqueous solution with anionic surfactant

```
XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: .05M SDS
QUANTUM YIELD:        0.01000
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.1880E+04
   300.00  *      0.00280     * 0.1210E+04
   302.50  *      0.00260     * 0.8800E+03
   305.00  *      0.00250     * 0.6490E+03
   307.50  *      0.00240     * 0.4780E+03
   310.00  *      0.00230     * 0.3860E+03
   312.50  *      0.00220     * 0.3750E+03
   315.00  *      0.00210     * 0.3050E+03
   317.50  *      0.00200     * 0.2390E+03
   320.00  *      0.00190     * 0.1430E+03
   323.10  *      0.00180     * 0.6950E+02
   330.00  *      0.00152     * 0.1160E+02
   340.00  *      0.00122     * 0.5800E+01
   350.00  *      0.00100     * 0.0000E+00
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED
```

XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: .05M SDS LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.196E-07	0.981E+04
		10.00	6.25	17.60	0.471E-07	0.409E+04
		20.00	7.12	16.73	0.172E-06	0.112E+04
		30.00	7.99	15.85	0.436E-06	0.441E+03
		40.00	8.91	14.94	0.109E-05	0.176E+03
		50.00	9.93	13.92	0.182E-05	0.106E+03
		60.00	11.75	12.10	0.233E-05	0.827E+02
	MIDDAY	60.09	11.92	11.92	0.233E-05	0.825E+02
		AVG RATE DURING DALITE(SEC**-1) 0.122E-05				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.581E-01				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.119E+2				
		NEAR SURFACE				
40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.196E-07	0.981E+04
		10.00	5.76	18.22	0.471E-07	0.409E+04
		20.00	6.65	17.33	0.172E-06	0.112E+04
		30.00	7.52	16.46	0.436E-06	0.441E+03
		40.00	8.39	15.59	0.109E-05	0.176E+03
		50.00	9.28	14.70	0.182E-05	0.106E+03
		60.00	10.24	13.74	0.233E-05	0.827E+02
		70.00	11.84	12.14	0.269E-05	0.716E+02
	MIDDAY	70.09	11.99	11.99	0.269E-05	0.715E+02
		AVG RATE DURING DALITE(SEC**-1) 0.139E-05				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.725E-01				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) [illegible]E+1				
		NEAR SURFACE				
40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.196E-07	0.981E+04
		10.00	7.18	16.20	0.471E-07	0.409E+04
		20.00	8.16	15.22	0.172E-06	0.112E+04
		30.00	9.30	14.08	0.436E-06	0.441E+03
		40.00	11.52	11.86	0.109E-05	0.176E+03
	MIDDAY	40.06	11.69	11.69	0.110E-05	0.175E+03
		AVG RATE DURING DALITE(SEC**-1) 0.602E-06				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.238E-01				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.291E+2				
		NEAR SURFACE				

```
 40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                 5.00    7.79   16.38   0.196E-07   0.981E+04
                10.00    8.31   15.85   0.471E-07   0.409E+04
                20.00    9.52   14.64   0.172E-06   0.112E+04
     MIDDAY     29.86   12.08   12.08   0.433E-06   0.445E+03

                AVG RATE DURING DALITE(SEC**-1)  0.277E-06
                RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.972E-02
                HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.713E+2
                NEAR SURFACE
```

System: Sevin on soil surfaces. The data here are calculated for conditions producing a "quantum yield" of 0.0003. See complete data for Sevin-soil experiments to obtain actual "quantum yields" for specific conditions.

```
XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: SOIL SURFACE
QUANTUM YIELD:          0.00030
INITIAL DEPTH:          0.00100
DEPTH INCREMENT:       10.00000
FINAL DEPTH:            5.00000
REFRACTIVE INDEX:       1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
    297.50  *      0.00280     * 0.1410E+04
    300.00  *      0.00280     * 0.9300E+03
    302.50  *      0.00260     * 0.7370E+03
    305.00  *      0.00250     * 0.5290E+03
    307.50  *      0.00240     * 0.4090E+03
    310.00  *      0.00230     * 0.3510E+03
    312.50  *      0.00220     * 0.3780E+03
    315.00  *      0.00210     * 0.2580E+03
    317.50  *      0.00200     * 0.2360E+03
    320.00  *      0.00190     * 0.1120E+03
    323.10  *      0.00180     * 0.5790E+02
    330.00  *      0.00152     * 0.1380E+02
    340.00  *      0.00122     * 0.0000E+00
    350.00  *      0.00100     * 0.0000E+00
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: CARBARYL
WATER IDENTIFICATION: SOIL SURFACE LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.332E-09	0.580E+06
		10.00	6.25	17.60	0.831E-09	0.232E+06
		20.00	7.12	16.73	0.362E-08	0.532E+05
		30.00	7.99	15.85	0.999E-08	0.193E+05
		40.00	8.91	14.94	0.270E-07	0.714E+04
		50.00	9.93	13.92	0.461E-07	0.417E+04
		60.00	11.75	12.10	0.593E-07	0.325E+04
	MIDDAY	60.09	11.92	11.92	0.593E-07	0.324E+04

AVG RATE DURING DALITE(SEC**-1) 0.305E-07
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.146E-02
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.476E+3
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.332E-09	0.580E+06
		10.00	5.76	18.22	0.831E-09	0.232E+06
		20.00	6.65	17.33	0.362E-08	0.532E+05
		30.00	7.52	16.46	0.999E-08	0.193E+05
		40.00	8.39	15.59	0.270E-07	0.714E+04
		50.00	9.28	14.70	0.461E-07	0.417E+04
		60.00	10.24	13.74	0.593E-07	0.325E+04
		70.00	11.84	12.14	0.687E-07	0.280E+04
	MIDDAY	70.09	11.99	11.99	0.688E-07	0.280E+04

AVG RATE DURING DALITE(SEC**-1) 0.350E-07
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.183E-02
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.[illegible]E+3
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.332E-09	0.580E+06
		10.00	7.18	16.20	0.831E-09	0.232E+06
		20.00	8.16	15.22	0.362E-08	0.532E+05
		30.00	9.30	14.08	0.999E-08	0.193E+05
		40.00	11.52	11.86	0.270E-07	0.714E+04
	MIDDAY	40.06	11.69	11.69	0.271E-07	0.711E+04

AVG RATE DURING DALITE(SEC**-1) 0.145E-07
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.575E-03
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.120E+4
NEAR SURFACE

```
40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                5.00    7.79   16.38   0.332E-09   0.560E+06
               10.00    8.31   15.85   0.831E-09   0.232E+06
               20.00    9.52   14.64   0.362E-08   0.532E+05
    MIDDAY     29.86   12.08   12.08   0.991E-08   0.194E+05

               AVG RATE DURING DAYLITE(SEC**-1)   0.623E-08
               RATE INTEGRATED OVER FULL DAY(DAY**-1)   0.218E-03
               HALF LIFE INTEGRATED OVER FULL DAY(DAYS)   0.317E+4
               NEAR SURFACE
```

System: Parathion in aqueous solution

```
XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: PURE WATER
QUANTUM YIELD:          0.00020
INITIAL DEPTH:          0.00100
DEPTH INCREMENT:       10.00000
FINAL DEPTH:            5.00000
REFRACTIVE INDEX:       1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.4800E+04
   300.00  *      0.00280     * 0.4500E+04
   302.50  *      0.00260     * 0.4250E+04
   305.00  *      0.00250     * 0.3750E+04
   307.50  *      0.00240     * 0.3250E+04
   310.00  *      0.00230     * 0.2750E+04
   312.50  *      0.00220     * 0.2350E+04
   315.00  *      0.00210     * 0.2000E+04
   317.50  *      0.00200     * 0.1600E+04
   320.00  *      0.00190     * 0.1550E+04
   323.10  *      0.00180     * 0.1400E+04
   330.00  *      0.00152     * 0.9500E+03
   340.00  *      0.00122     * 0.5500E+03
   350.00  *      0.00100     * 0.4000E+03
LATITUDE 40 WAS SELECTED.
SEASON # 1 IS SU
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

```
XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION:  PURE WATER                    LONGITUDE: 90.00
 LAT.   SEASON SOLAR    MORN     EVEN       RATE      HALF LIFE
               ALT.     TIME     TIME       /SEC        HOURS
 40.00 SUMMER    0.00    4.74    19.24  0.000E+00   0.000E+00
                 5.00    5.29    18.69  0.699E-07   0.275E+04
                10.00    5.76    18.22  0.170E-06   0.113E+04
                20.00    6.65    17.33  0.458E-06   0.420E+03
                30.00    7.52    16.46  0.874E-06   0.220E+03
                40.00    8.39    15.59  0.135E-05   0.143E+03
                50.00    9.28    14.70  0.181E-05   0.107E+03
                60.00   10.24    13.74  0.219E-05   0.878E+02
                70.00   11.84    12.14  0.245E-05   0.787E+02
    MIDDAY      70.09   11.99    11.99  0.245E-05   0.786E+02

                AVG RATE DURING DALITE(SEC**-1)  0.144E-05
                RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.752E-01
                HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.921E+1
                NEAR SURFACE
```

System: Parathion in aqueous solution with cationic surfactant

```
XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: .05M CTAB
QUANTUM YIELD:          0.00060
INITIAL DEPTH:          0.00100
DEPTH INCREMENT:       10.00000
FINAL DEPTH:            5.00000
REFRACTIVE INDEX:       1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.6250E+04
   300.00  *      0.00260     * 0.5800E+04
   302.50  *      0.00260     * 0.5150E+04
   305.00  *      0.00250     * 0.4500E+04
   307.50  *      0.00240     * 0.3800E+04
   310.00  *      0.00230     * 0.3100E+04
   312.50  *      0.00220     * 0.2900E+04
   315.00  *      0.00210     * 0.2200E+04
   317.50  *      0.00200     * 0.1850E+04
   320.00  *      0.00190     * 0.1600E+04
   323.10  *      0.00180     * 0.1450E+04
   330.00  *      0.00152     * 0.9000E+03
   340.00  *      0.00122     * 0.6000E+03
   350.00  *      0.00100     * 0.4500E+03
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDES AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: .05M CTAR LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.210E-06	0.918E+03
		10.00	6.25	17.60	0.505E-06	0.381E+03
		20.00	7.12	16.73	0.137E-05	0.140E+03
		30.00	7.99	15.85	0.263E-05	0.731E+02
		40.00	8.91	14.94	0.414E-05	0.465E+02
		50.00	9.93	13.92	0.558E-05	0.345E+02
		60.00	11.75	12.10	0.678E-05	0.284E+02
	MIDDAY	60.09	11.92	11.92	0.679E-05	0.284E+02

AVG RATE DURING DALITE(SEC**-1) 0.405E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.193E+00
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.359E+1
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.220E-06	0.876E+03
		10.00	5.76	18.22	0.535E-06	0.360E+03
		20.00	6.65	17.33	0.144E-05	0.133E+03
		30.00	7.52	16.46	0.277E-05	0.695E+02
		40.00	8.39	15.59	0.430E-05	0.448E+02
		50.00	9.28	14.70	0.577E-05	0.333E+02
		60.00	10.24	13.74	0.703E-05	0.274E+02
		70.00	11.84	12.14	0.785E-05	0.245E+02
	MIDDAY	70.09	11.99	11.99	0.785E-05	0.245E+02

AVG RATE DURING DALITE(SEC**-1) 0.461E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.241E+00
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.288E+1
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.230E-06	0.837E+03
		10.00	7.18	16.20	0.567E-06	0.340E+03
		20.00	8.16	15.22	0.152E-05	0.127E+03
		30.00	9.30	14.08	0.291E-05	0.661E+02
		40.00	11.52	11.86	0.445E-05	0.432E+02
	MIDDAY	40.06	11.69	11.69	0.446E-05	0.431E+02

AVG RATE DURING DALITE(SEC**-1) 0.288E-05
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.114E+00
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.608E+1
NEAR SURFACE

```
 40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                 5.00    7.79   16.38   0.218E-06   0.881E+03
                10.00    8.31   15.85   0.531E-06   0.362E+03
                20.00    9.52   14.64   0.144E-05   0.134E+03
     MIDDAY     29.86   12.08   12.08   0.274E-05   0.703E+02

                AVG RATE DURING DALITE(SEC**-1)  0.188E-05
                RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.658E-01
                HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.105E+2
                NEAR SURFACE
```

System: Parathion in aqueous solution with anionic surfactant

```
XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: .05M SDS
QUANTUM YIELD:        0.00100
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.6350E+04
   300.00  *      0.00280     * 0.5850E+04
   302.50  *      0.00260     * 0.5500E+04
   305.00  *      0.00250     * 0.4800E+04
   307.50  *      0.00240     * 0.4200E+04
   310.00  *      0.00230     * 0.3700E+04
   312.50  *      0.00220     * 0.3400E+04
   315.00  *      0.00210     * 0.2800E+04
   317.50  *      0.00200     * 0.2450E+04
   320.00  *      0.00190     * 0.2100E+04
   323.10  *      0.00180     * 0.1850E+04
   330.00  *      0.00152     * 0.1300E+04
   340.00  *      0.00122     * 0.9500E+03
   350.00  *      0.00100     * 0.6500E+03
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDE AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: .05M SDS LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.511E-06	0.377E+03
		10.00	6.25	17.60	0.122E-05	0.158E+03
		20.00	7.12	16.73	0.327E-05	0.588E+02
		30.00	7.99	15.85	0.620E-05	0.310E+02
		40.00	8.91	14.94	0.965E-05	0.200E+02
		50.00	9.93	13.92	0.129E-04	0.149E+02
		60.00	11.75	12.10	0.156E-04	0.123E+02
	MIDDAY	60.09	11.92	11.92	0.156E-04	0.123E+02
		AVG RATE DURING DALITE(SEC**-1) 0.937E-05				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.447E+00				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.155E+1				
		NEAR SURFACE				
40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.533E-06	0.361E+03
		10.00	5.76	18.22	0.129E-05	0.150E+03
		20.00	6.65	17.33	0.343E-05	0.562E+02
		30.00	7.52	16.46	0.649E-05	0.297E+02
		40.00	8.39	15.59	0.997E-05	0.193E+02
		50.00	9.28	14.70	0.133E-04	0.145E+02
		60.00	10.24	13.74	0.161E-04	0.120E+02
		70.00	11.84	12.14	0.179E-04	0.107E+02
	MIDDAY	70.09	11.99	11.99	0.179E-04	0.107E+02
		AVG RATE DURING DALITE(SEC**-1) 0.106E-04				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.553E+00				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.125E+1				
		NEAR SURFACE				
40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.555E-06	0.347E+03
		10.00	7.18	16.20	0.136E-05	0.142E+03
		20.00	8.16	15.22	0.359E-05	0.536E+02
		30.00	9.30	14.08	0.678E-05	0.284E+02
		40.00	11.52	11.86	0.103E-04	0.187E+02
	MIDDAY	40.06	11.69	11.69	0.103E-04	0.187E+02
		AVG RATE DURING DALITE(SEC**-1) 0.669E-05				
		RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.265E+00				
		HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.262E+1				
		NEAR SURFACE				

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40.00 WINTER    0.00    7.21   16.95   0.000E+00   0.000E+00
                5.00    7.79   16.38   0.530E-06   0.363E+03
               10.00    8.31   15.85   0.128E-05   0.150E+03
               20.00    9.52   14.64   0.341E-05   0.565E+02
    MIDDAY     29.86   12.08   12.08   0.642E-05   0.300E+02

               AVG RATE DURING DAYLITE(SEC**-1)  0.441E-05
               RATE INTEGRATED OVER FULL DAY(DAY**-1)  0.155E+00
               HALF LIFE INTEGRATED OVER FULL DAY(DAYS)  0.447E+1
               NEAR SURFACE
```

System: Parathion on soil surfaces. The data here are calculated for conditions producing a "quantum yield" of 0.0001. See complete data for Parathion-soil experiments to obtain actual "quantum yields" for specific conditions.

```
XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: SOIL SURFACE
QUANTUM YIELD:        0.00010
INITIAL DEPTH:        0.00100
DEPTH INCREMENT:     10.00000
FINAL DEPTH:          5.00000
REFRACTIVE INDEX:     1.34000
WAVE LENGTH*WATER ABSORPTION*  EPSILON
   (NM)
   297.50  *      0.00280     * 0.4800E+04
   300.00  *      0.00280     * 0.4500E+04
   302.50  *      0.00260     * 0.4250E+04
   305.00  *      0.00250     * 0.3750E+04
   307.50  *      0.00240     * 0.3250E+04
   310.00  *      0.00230     * 0.2750E+04
   312.50  *      0.00220     * 0.2350E+04
   315.00  *      0.00210     * 0.2000E+04
   317.50  *      0.00200     * 0.1600E+04
   320.00  *      0.00190     * 0.1550E+04
   323.10  *      0.00180     * 0.1400E+04
   330.00  *      0.00152     * 0.9500E+03
   340.00  *      0.00122     * 0.5500E+03
   350.00  *      0.00100     * 0.4000E+03
LATITUDE 40 WAS SELECTED.
ALL SEASONS WERE SELECTED.
LONGITUDE SELECTED:  90.00
TIME-OF-DAY COMPUTATIONS ARE REQUESTED.
TYPICAL EPHEMERIDS AND OZONE VALUES WERE SELECTED.
```

XENOBIOTIC NAME: PARATHION
WATER IDENTIFICATION: SOIL SURFACE LONGITUDE: 90.00

LAT.	SEASON	SOLAR ALT.	MORN TIME	EVEN TIME	RATE /SEC	HALF LIFE HOURS
40.00	SPRING	0.00	5.29	18.55	0.000E+00	0.000E+00
		5.00	5.81	18.04	0.334E-07	0.577E+04
		10.00	6.25	17.60	0.804E-07	0.239E+04
		20.00	7.12	16.73	0.218E-06	0.884E+03
		30.00	7.99	15.85	0.416E-06	0.463E+03
		40.00	8.91	14.94	0.651E-06	0.296E+03
		50.00	9.93	13.92	0.874E-06	0.220E+03
		60.00	11.75	12.10	0.106E-05	0.182E+03
	MIDDAY	60.09	11.92	11.92	0.106E-05	0.181E+03

AVG RATE DURING DALITE(SEC**-1) 0.635E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.303E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.229E+2
NEAR SURFACE

40.00	SUMMER	0.00	4.74	19.24	0.000E+00	0.000E+00
		5.00	5.29	18.69	0.349E-07	0.551E+04
		10.00	5.76	18.22	0.851E-07	0.226E+04
		20.00	6.65	17.33	0.229E-06	0.840E+03
		30.00	7.52	16.46	0.437E-06	0.441E+03
		40.00	8.39	15.59	0.675E-06	0.285E+03
		50.00	9.28	14.70	0.903E-06	0.213E+03
		60.00	10.24	13.74	0.110E-05	0.176E+03
		70.00	11.84	12.14	0.122E-05	0.157E+03
	MIDDAY	70.09	11.99	11.99	0.122E-05	0.157E+03

AVG RATE DURING DALITE(SEC**-1) 0.720E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.376E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.184E+2
NEAR SURFACE

40.00	FALL	0.00	6.19	17.19	0.000E+00	0.000E+00
		5.00	6.72	16.66	0.366E-07	0.526E+04
		10.00	7.18	16.20	0.901E-07	0.214E+04
		20.00	8.16	15.22	0.241E-06	0.799E+03
		30.00	9.30	14.08	0.458E-06	0.420E+03
		40.00	11.52	11.86	0.697E-06	0.276E+03
	MIDDAY	40.06	11.69	11.69	0.699E-06	0.275E+03

AVG RATE DURING DALITE(SEC**-1) 0.452E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.179E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.387E+2
NEAR SURFACE

40.00 WINTER	0.00	7.21	16.95	0.000E+00	0.000E+00
	5.00	7.79	16.38	0.348E-07	0.554E+04
	10.00	8.31	15.85	0.845E-07	0.228E+04
	20.00	9.52	14.64	0.228E-06	0.845E+03
MIDDAY	29.86	12.08	12.08	0.432E-06	0.446E+03

AVG RATE DURING DALITE(SEC**-1) 0.296E-06
RATE INTEGRATED OVER FULL DAY(DAY**-1) 0.104E-01
HALF LIFE INTEGRATED OVER FULL DAY(DAYS) 0.666E+2
NEAR SURFACE